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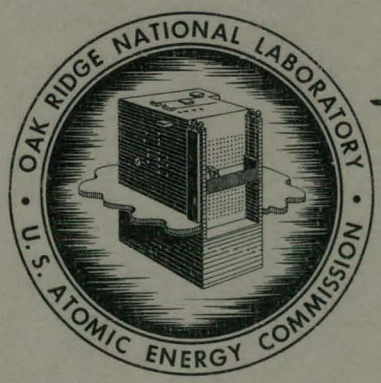

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Chemical Development Section A

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ABSTRACT

Aqueous slurries of thorium oxide and thorium oxide containing uranium were investigated for their catalytic activity for the reaction of hydrogen and oxygen to form water. Pure thorium oxide, thorium-uranium oxide mixed crystals prepared by calcining coprecipitated oxalates, and thorium oxide with uranium oxide sorbed on the surface were used after calcining at 650°, 800°, and 1000°. The reaction rates were found to be first order with respect to hydrogen pressure and zero order with respect to oxygen pressure in all cases at temperatures from 230 to 300° and total gas pressures from 100 to 2000 p.s.i. For the pure thorium oxide an average activation energy of 41 kcal./mole and an average frequency factor of 4.6×10^8 moles/p.s.i. H_2-hr.-g of ThO_2 were found. Addition of uranium lowered both factors, the maximum effect giving a ΔE_a of ~14 kcal. with an A of $\sim 10^{-2}$. Actual rates for all catalysts were within one order of magnitude when compared on a unit surface area basis. This compensation effect was explained on the basis of a two-site process, one site being related to the uranium concentration on the catalyst surface and the other characteristic of pure thorium oxide. A few tests on uranium trioxide slurries gave initial fast rates followed by slow ones, the change being accompanied by reduction of the surface uranium under the experimental conditions. The apparent activation energy for both surface conditions was 26 kcal./mole based on first order rate constants with frequency factors of 2.2×10^4 and 2.5×10^3 moles/p.s.i. H_2-hr.-g. for the initial and final rates, respectively.

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CHAPTER I

INTRODUCTION

The reaction of hydrogen with oxygen to form water has for some time received considerable attention, and papers on this subject still appear frequently in the literature. Although simple on the surface, the reaction is amazingly complex. Hinshelwood and Williamson published a monograph on the subject in 1934[1] in which they summarized the results of other researchers. More recent review articles on the homogeneous reaction have been published by Hinshelwood[2] and by Smith.[3] The reaction has also been investigated as it occurs on the surfaces of many metals and oxides.

With the advent of nuclear reactors of the homogeneous type in which a fissile or fertile material is dissolved or suspended in an aqueous medium, a new aspect of the problem appeared. Radiolysis of the water in these systems leads to the formation of hydrogen and oxygen gases which must be reacted again to form water before they accumulate and become a threat to reactor safety or control.[4] The problem has been solved for reactor systems using uranyl sulfate solutions by the addition of copper sulfate.[5] The copper ion acts as a homogeneous catalyst providing complete recombination in the liquid phase.

The problem in the case of reactor systems using thorium oxide or thorium oxide-uranium oxide slurries as breeding blankets or as fuels is

more complex. Copper sulfate is not suitable, and other catalysts that have been investigated apparently depend on a certain type of support surface which is not always attained.[6] Work has been done on the addition of other catalysts, but only cursory attention was paid to systems containing only thorium oxide or thorium-uranium oxides. The work on both solutions and slurries was reviewed by McCord in 1956 in a classified document which has since been declassified.[7]

The study reported here was undertaken to provide basic kinetic data on the recombination reaction using typical slurries without the addition of any other catalyst. These data will provide a firm base line for studies with other catalysts, and are necessary as well for the proper interpretation of in-pile gas production rate tests currently being carried out at Oak Ridge National Laboratory.[8]

CHAPTER II

EXPERIMENTAL

A. Preparation of Catalysts

1. Thorium Oxide

The thorium oxide used was from a single batch of material prepared by the Chemical Technology Division Pilot Plant Section. The material was prepared by precipitating thorium oxalate from a solution of thorium nitrate with oxalic acid. After being filtered and washed, the thorium oxalate was air dried and heated successively at 180°, 380°, and 650° to convert it to thorium oxide. Additional twenty-four hour calcinations were made at 800° and 1000° in a laboratory muffle furnace equipped with a Minneapolis Honeywell 0°-1600° pyrometer and a platinum-platinum rhodium thermocouple.

2. Thorium-Uranium Oxide Mixed Crystals

Mixed thorium-uranium oxide particles in which the uranium was distributed throughout the crystal were prepared by coprecipitating thorium oxalate and uranium(IV) oxalate by the method reported by McBride, Allred, Schilling, and Jones.[9] The oxalate was then decomposed by a multistage calcination similar to that used above for the pure thorium oxide preparation. Final calcination temperatures were again 650°, 800°, and 1000°.

3. Thorium Oxide with Adsorbed Uranium Oxide

The mixed thorium-uranium oxide in which the uranium oxide was placed on the thorium oxide surface was prepared by the simple mixing of the 650° calcined thorium oxide and uranium trioxide followed by refluxing overnight in water. The slight solubility of the uranium trioxide, perhaps with the aid of a small nitrate impurity, allows it to distribute itself on the surface of the thorium oxide,[10] the deposition being accompanied by a change of color from white to peach. The material was then dried and split into three batches which were recalcined for twenty-four hours at 650°, 800°, and 1000°, respectively.

B. Properties of the Catalysts

1. Chemical Composition

Dried samples of each catalyst preparation used were analyzed for thorium and uranium. The results are given in Table I.

2. Specific Surface Area

The specific surface area for each catalyst preparation was measured by the B.E.T. method with nitrogen gas. The results are given in Table II. The more marked reduction of specific surface with calcination temperature noted for the uranium bearing materials is a result of the lowering of the sintering temperature caused by the presence of the uranium oxide. The effect is most pronounced in the case of the material

TABLE I

CHEMICAL ANALYSES OF CATALYST PREPARATIONS

Material	Calcination Temperature	Th, %	U, %
Thorium oxide	650°	86.8	0
	800°	87.3	0
	1000°	87.6	0
Thorium-uranium oxide mixed crystals	650°	83.5	4.2
	800°	83.7	4.2
	1000°	84.3	4.3
Thorium oxide-uranium oxide coated	650°	83.2	3.6
	800°	83.5	3.6
	1000°	84.0	3.6

TABLE II

SPECIFIC SURFACE AREA OF CATALYST PREPARATIONS

Material	Surface Area, $m.^2/g.$ Calcined at 650°	800°	1000°
Thorium oxide	32.2	14.3	4.8
Thorium oxide-uranium oxide mixed crystals	17.6	6.0	1.5
Thorium oxide-uranium oxide coated	26.0	18.5	1.9

prepared by the coprecipitation technique.

3. Electron Micrographs

Electron micrographs were made of each of the catalyst preparations using a replica technique to bring out surface structure[11] (see Figures 1 through 9). The pictures show marked sintering in the case of the thorium oxide-uranium oxide mixed crystals; this becomes extremely pronounced for the 1000° calcined material. The particles also seem to be of a more uniform size, with a noticeable lack of fines. The pure thorium oxide and the thorium oxide coated with uranium oxide look much alike, as expected since they were prepared from one batch of 650° calcined thorium oxide. Some sintering appears at the 1000° calcination temperature for the coated material, perhaps indicating diffusion of uranium into the thorium oxide lattice with a resultant lowering of the sintering temperature.

4. Particle Size Distribution

Particle size measurements were made on each catalyst by a sedimentation technique.[12] The results are given in Table III. It is noted that the pure thorium oxide particle size distribution does not change with calcination temperature, while the uranium-bearing materials show an increase in the number of large particles when calcined at 1000°, thus supporting the observations made from the photomicrographs. The mixed crystals grew in a uniform manner, while the material prepared by adsorption

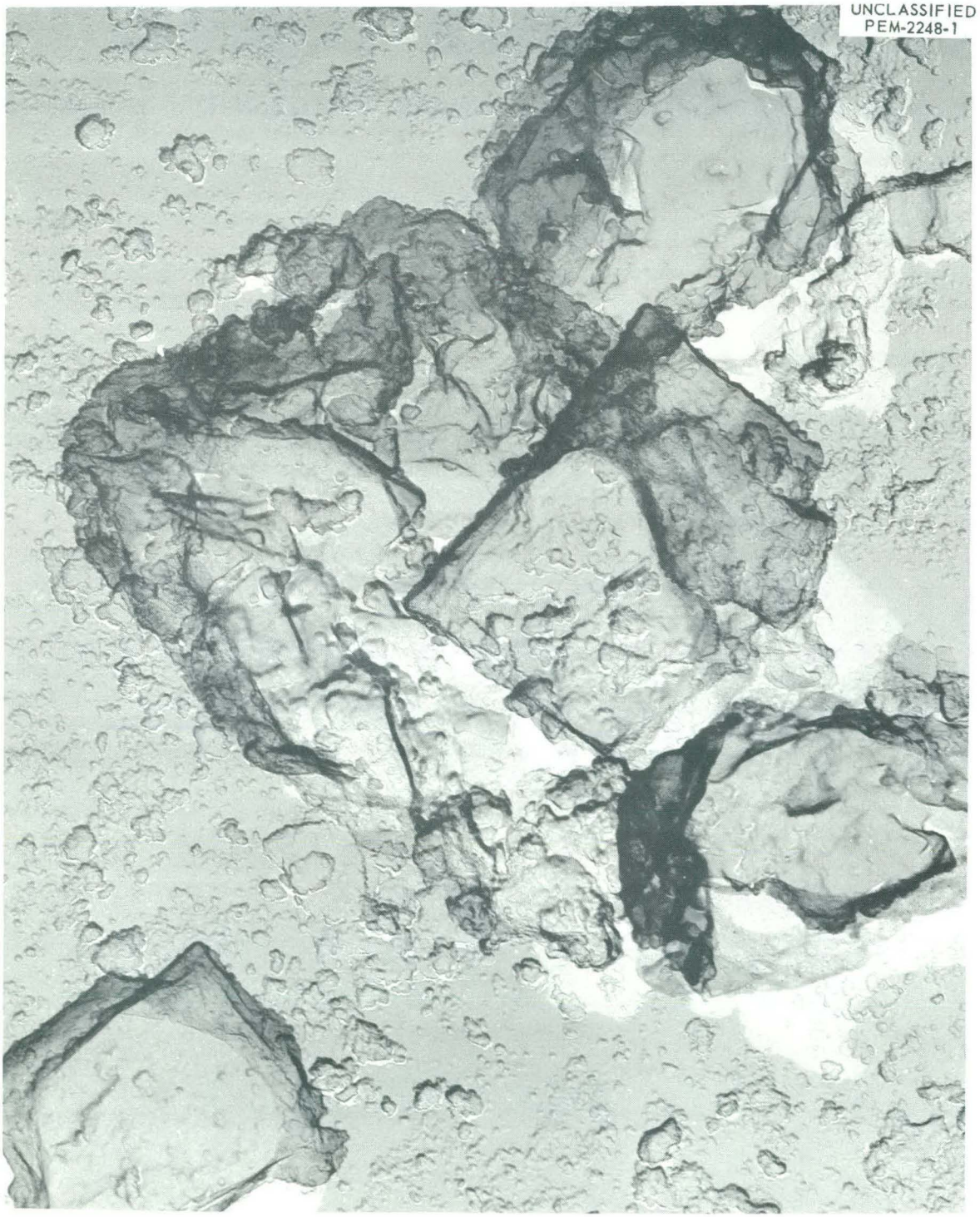

Fig. 1. Photomicrograph of replica of 650° calcined thorium oxide. 32,000X

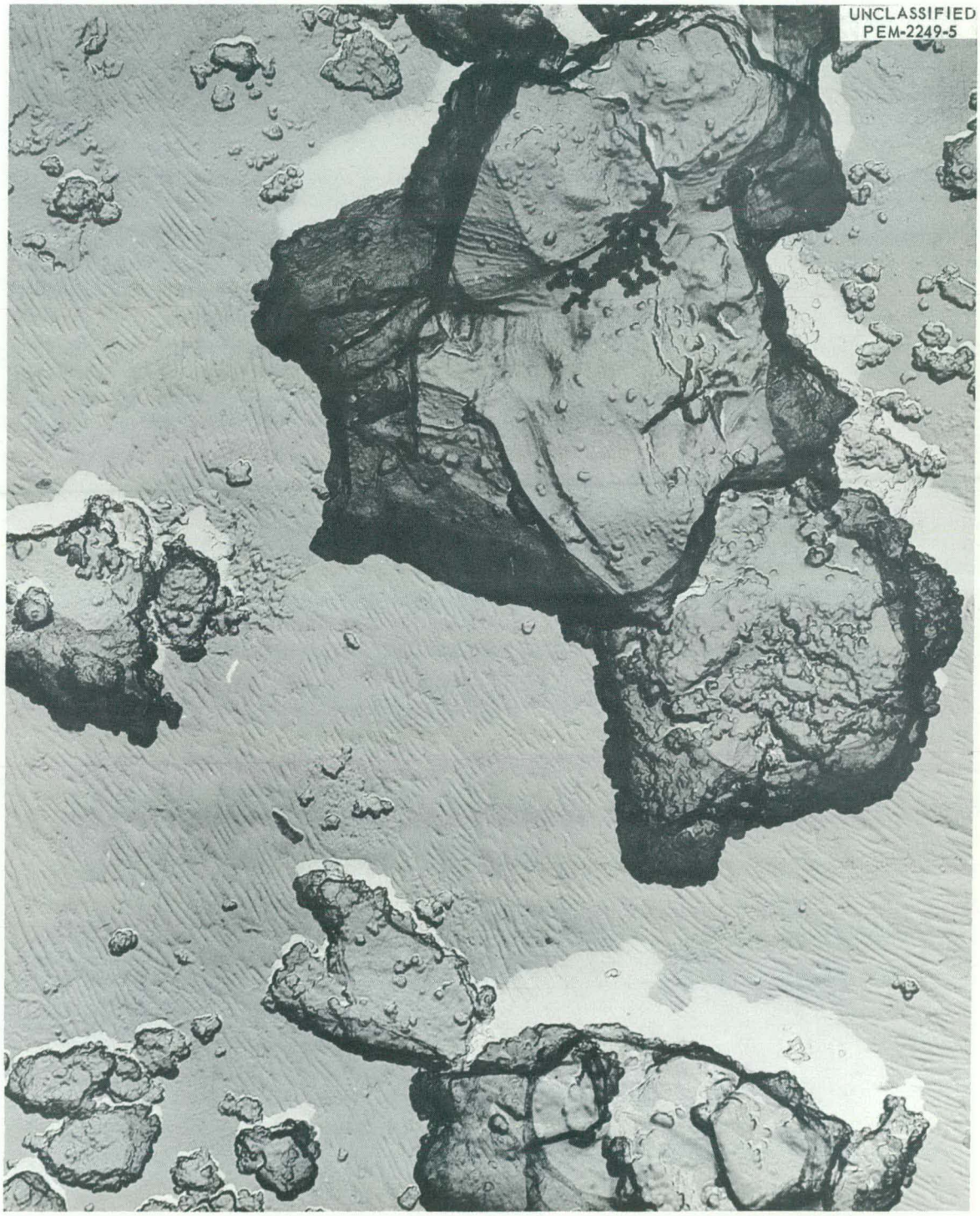

Fig. 2. Photomicrograph of replica of 800° calcined thorium oxide. 32,000X

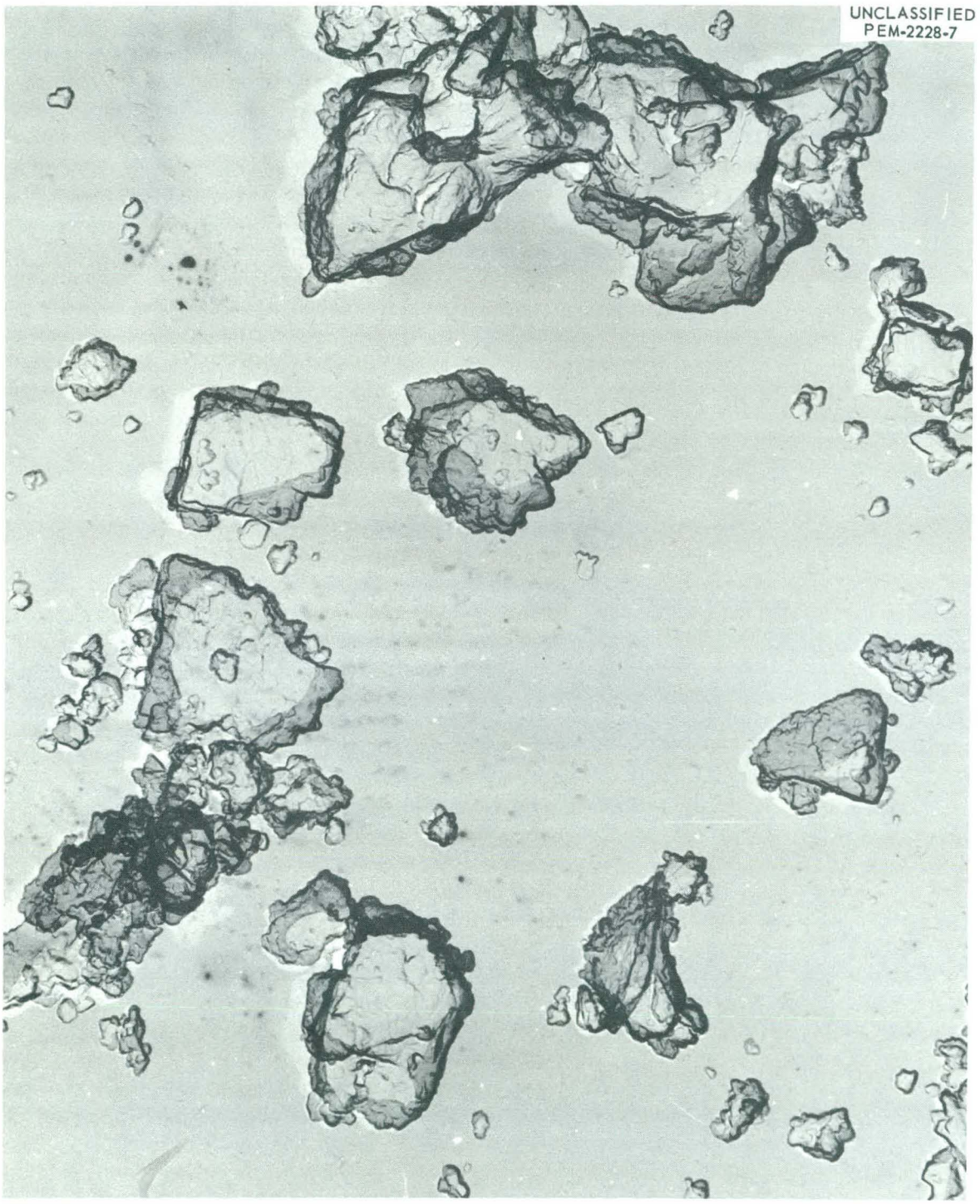

Fig. 3. Photomicrograph of replica of 1000° calcined thorium oxide. 32,000X

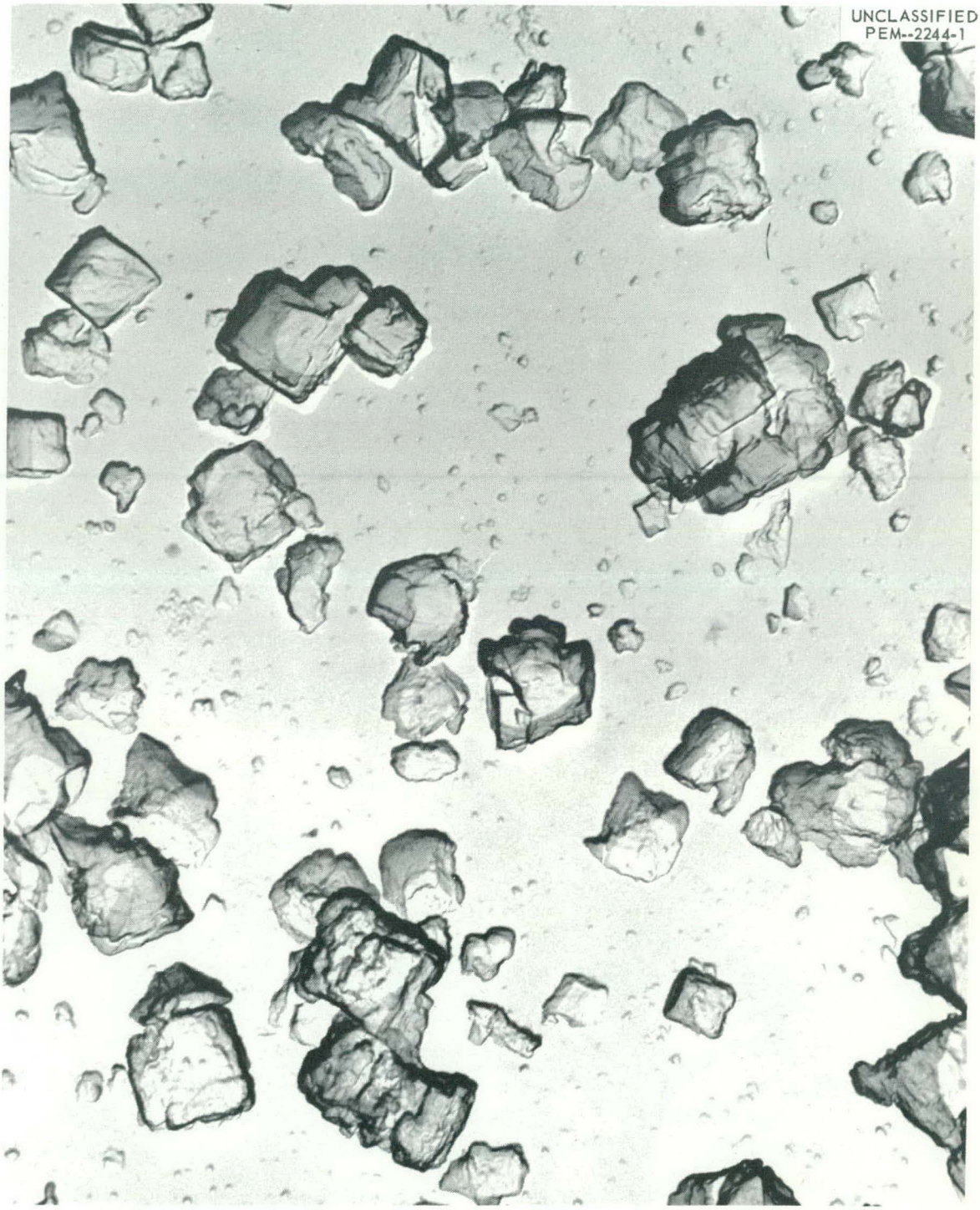

Fig. 4. Photomicrograph of replica of 650° calcined thorium-uranium oxide mixed crystals. 32,000X

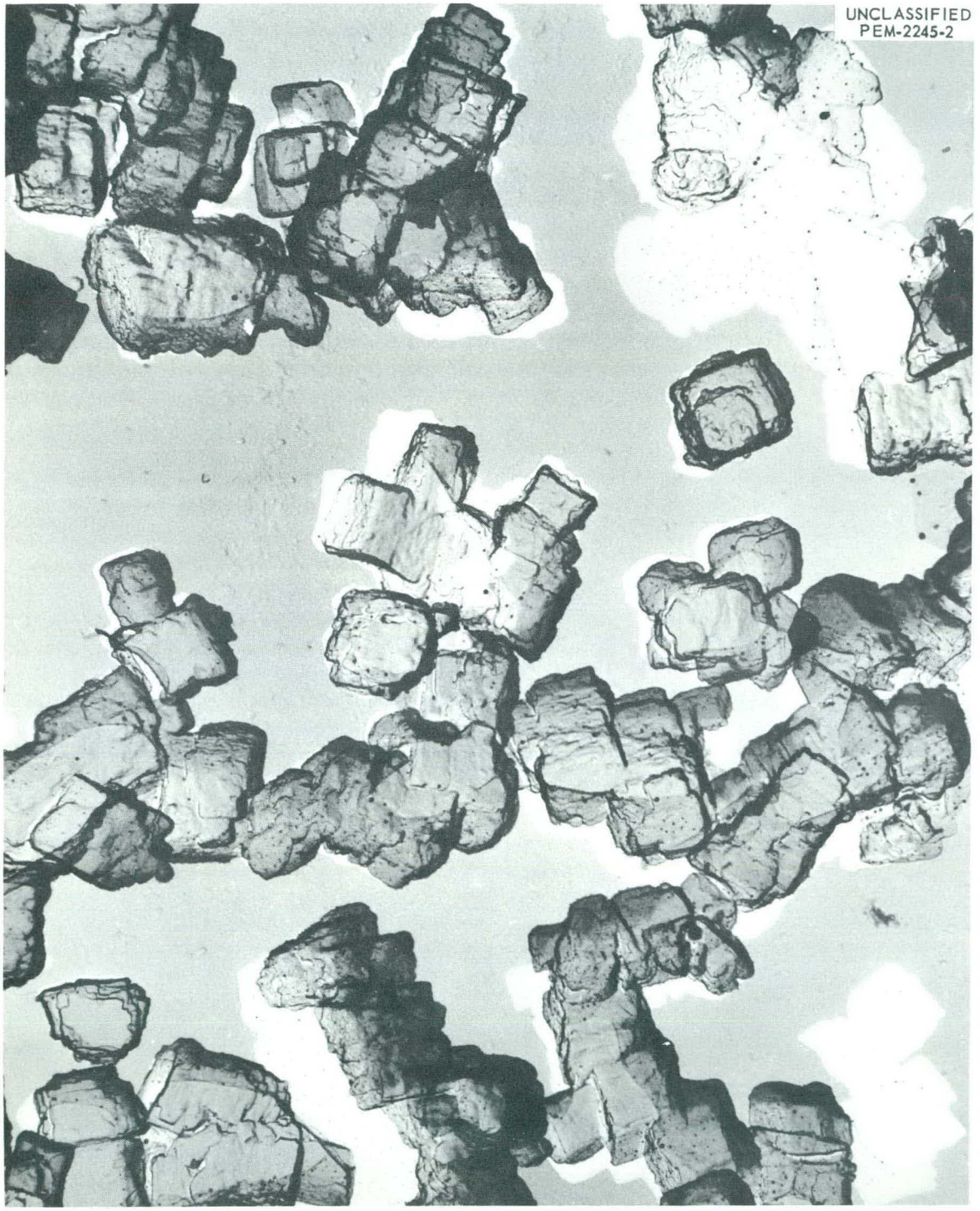

Fig. 5. Photomicrograph of replica of 800° calcined thorium-uranium oxide mixed crystals. 32,000X

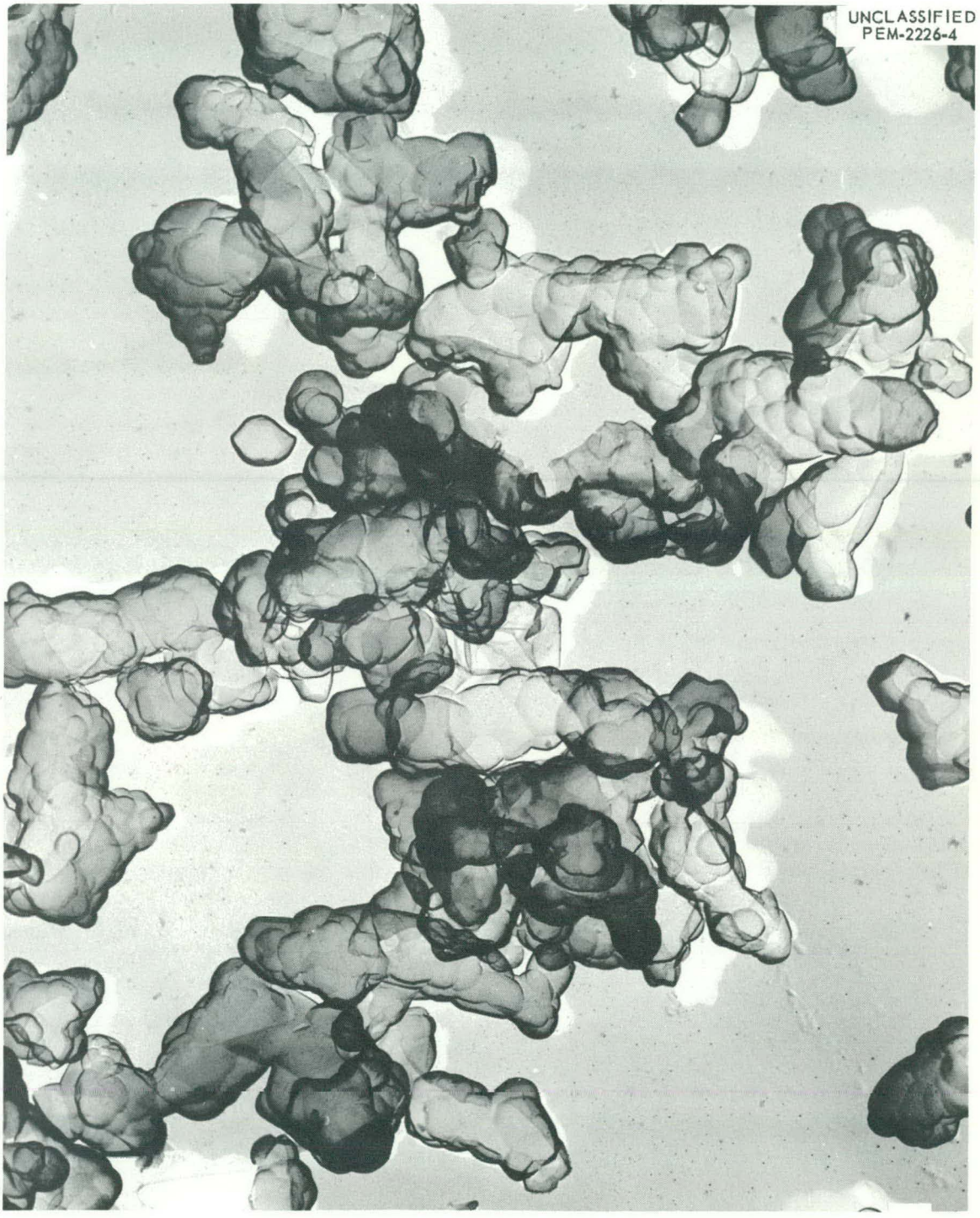

Fig. 6. Photomicrograph of replica of 1000° calcined thorium-uranium oxide mixed crystals. 32,000X

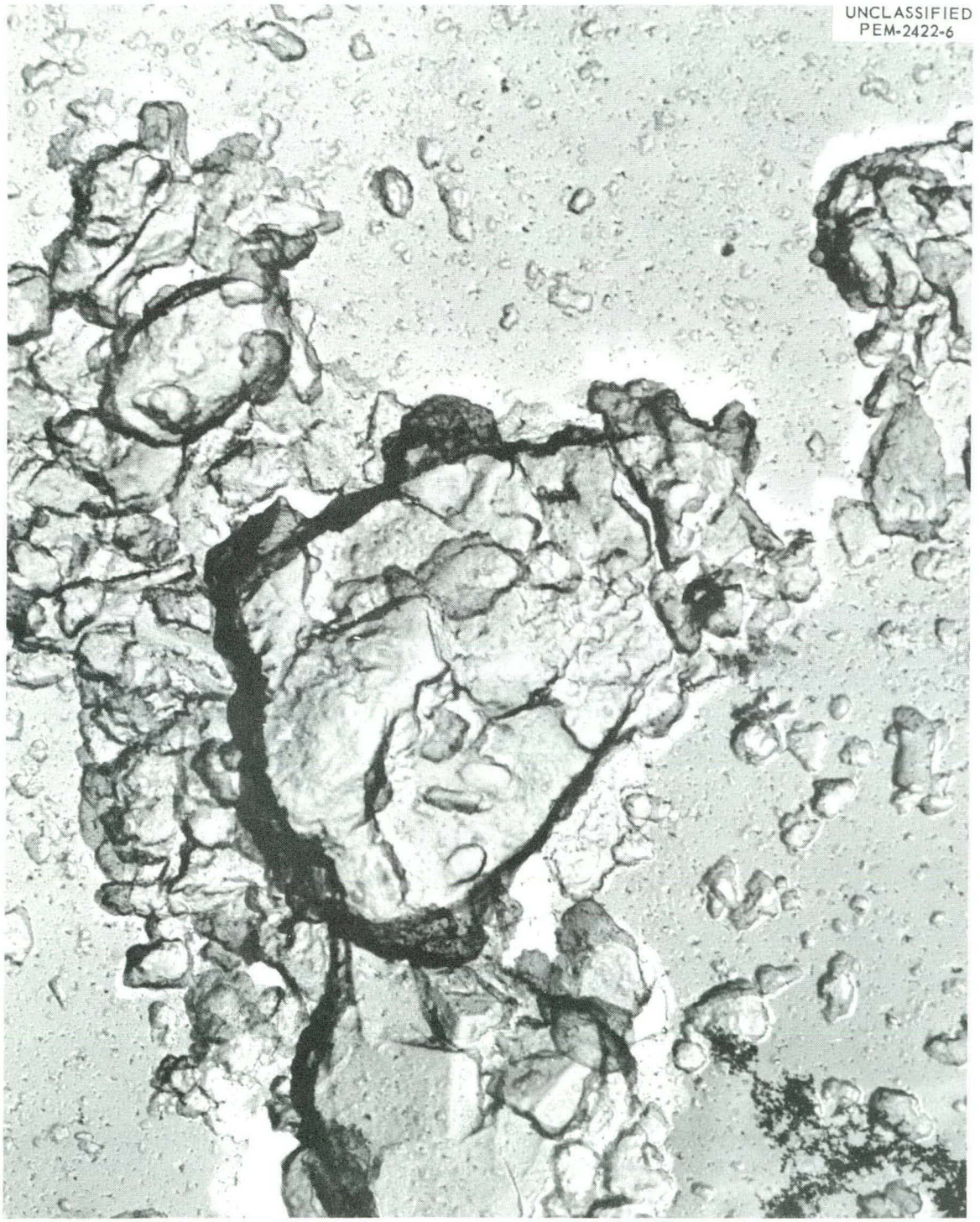

Fig. 7. Photomicrograph of replica of 650° calcined thorium oxide with adsorbed uranium oxide. 20,000X

Fig. 8. Photomicrograph of replica of 800° calcined thorium oxide with adsorbed uranium oxide. 20,000X

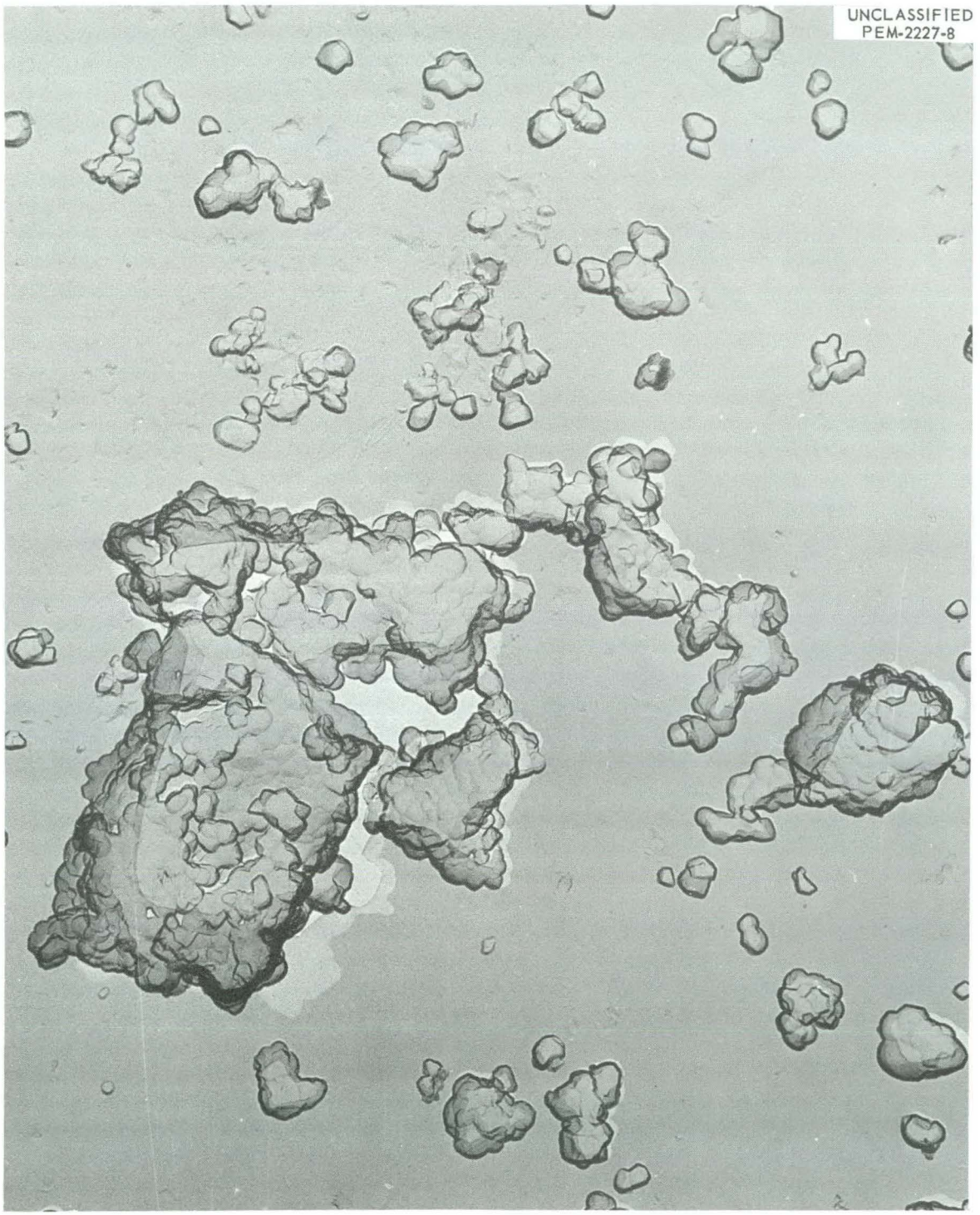

Fig. 9. Photomicrograph of replica of 1000° calcined thorium oxide with adsorbed uranium oxide. 32,000X

TABLE III

PARTICLE SIZE DISTRIBUTION OF CATALYST PREPARATIONS

Material	Calcination Temperature	Weight Per Cent Less Than Stated Size			
		10 μ	5 μ	2 μ	1 μ
Thorium oxide	650°	88	74	47	22
	800°	89	77	44	18
	1000°	87	70	43	16
Thorium oxide-	650°	98+	94	69	30
adsorbed uranium	800°	98+	94	67	29
oxide	1000°	83	82	79	28
Thorium oxide-	650°	98+	98	96	60
uranium oxide	800°	98+	97	96	64
mixed crystals	1000°	98+	93	58	21

apparently made large particles at the expense of those in the 2 to 5 micron region, which resulted in an abnormal distribution. No difference was noted in the particle size distribution between the 650° and 800° calcined materials. The particles of the mixed crystals of thorium oxide-uranium oxide were found by the sedimentation analysis to be of more uniform size. This also was observed in the electron micrographs.

C. Other Materials

1. Gases

Hydrogen and oxygen were used as obtained in commercial gas cylinders.

2. Water

The water used in all experiments was from the laboratory distilled water supply.

D. Apparatus

A schematic diagram of the equipment used is given in Figure 10. The important features are described below.

1. Reaction Vessels

The reaction vessels (Figure 11) were machined at the Oak Ridge National Laboratory machine shops out of type 347 stainless steel. The

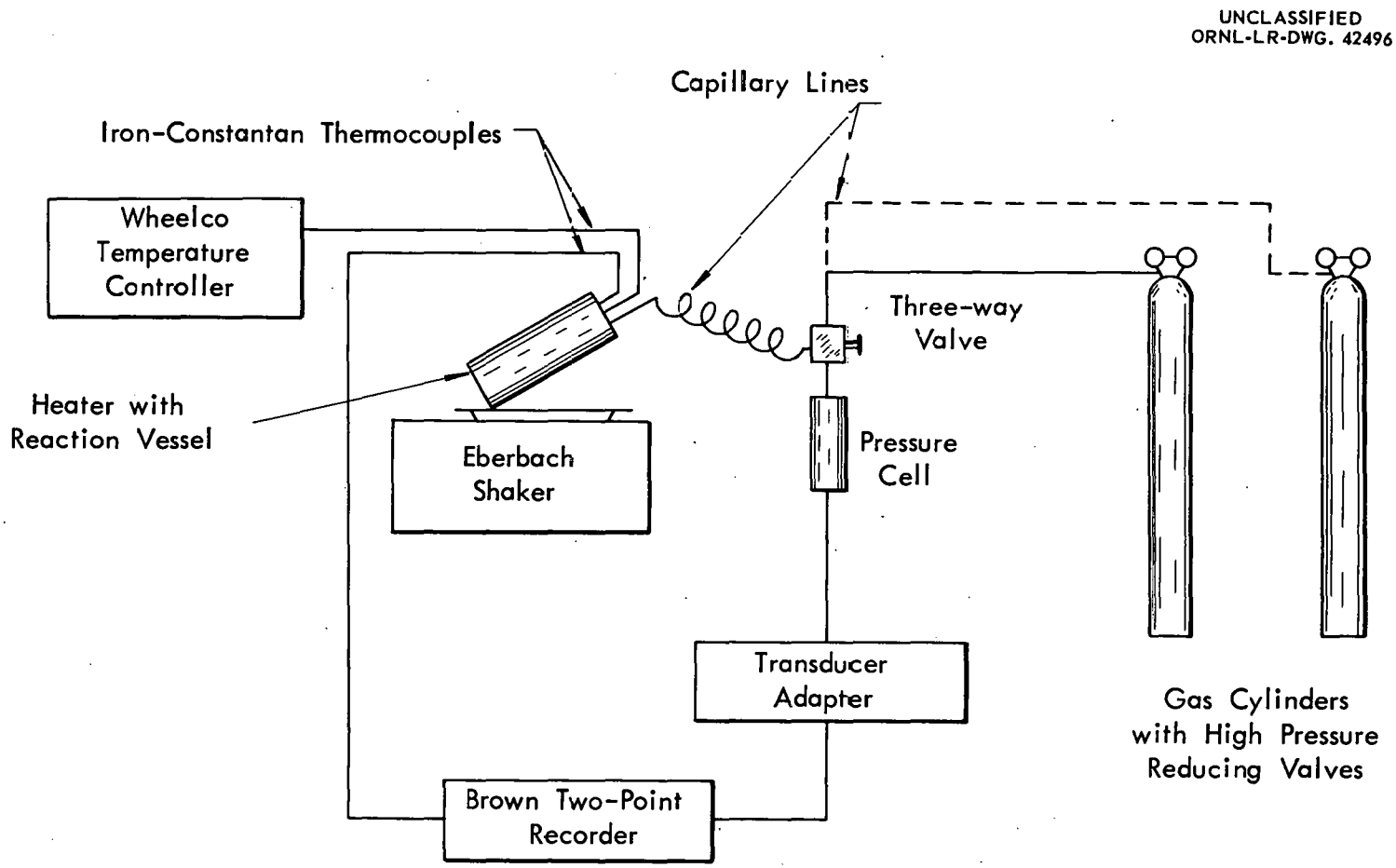

Fig. 10. Diagram of equipment.

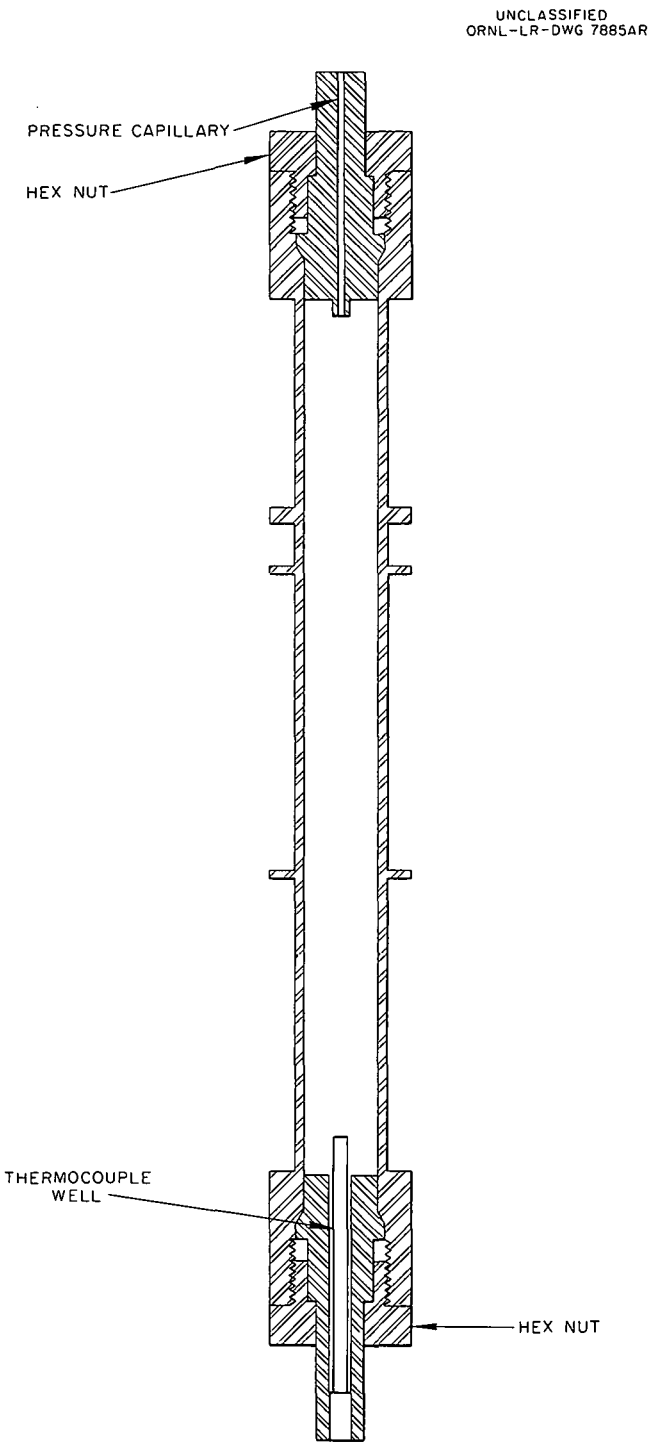

Fig. 11. Reaction vessel.

vessels, identical to those used in in-pile experiments by Krohn,[13] were cylinders approximately 19 cm. long and 1 cm. in inside diameter, open at both ends. The ends were closed with high-pressure cone type fittings held in place with carbon steel gland nuts.

An iron-Constantan thermocouple was welded into a small well in the bottom fitting for measuring the slurry temperature.

In the upper fitting was welded a 20-mil-I.D. 35-mil-O.D. stainless steel capillary tube used to transmit pressure from the vessel to the pressure gauge.

2. Temperature Measurement and Control

All temperatures were measured with iron-Constantan thermocouples made from 30 gauge B. and S. duplex wire purchased from Leeds and Northrup Instrument Company.

Slurry temperature was continuously monitored on one pen of a two-pen Minneapolis-Honeywell recording potentiometer which had been calibrated with a Rubicon No. 2733 potentiometer.

The vessel temperature was controlled with a Wheelco model 402 pyrometer having a range of 0° to 400°. A Variac was used to control the heater current at a maximum of 4 amp. By placing the pyrometer thermocouple between the reaction vessel and the heater wall, the slurry temperature was maintained to within $\pm 1^{\circ}$ in the temperature range 200° to 300°.

3. Pressure Measurement

Pressure measurements were continuously recorded by the use of a 0 to 5000 p.s.i. Baldwin SR-4 pressure cell whose output was fed through a transducer calibration adapter to the second pen of the recording potentiometer mentioned above. The system, when calibrated with a dead-weight gauge, was found to be linear and to read within 1 per cent of the correct value over its entire range (Figure 12, Table IV). The sensitivity of the recording potentiometer could be adjusted to 2500 p.s.i. or 5000 p.s.i. full scale reading by use of a range selector switch on the adapter.

4. Heating and Shaking Mechanisms

The autoclave was heated to the desired temperature in a heater made of heavy-walled aluminum tubing wound noninductively with asbestos-insulated Nichrome wire. The heater was clamped on an Eberbach model 55 variable-speed shaking apparatus at an angle of approximately 30 degrees to the horizontal. The speed of the shaker was continuously adjustable from 0 to 320 cycles per minute with a constant stroke of 3.9 cm. Visual observations at room temperature, using a glass tube the same size as the autoclave, showed that at the higher speeds the shaking was sufficient to suspend the solids in a few minutes.

An alternative method of stirring with an electromagnetically energized dasher, for which the reaction vessel was originally designed, was tried but discarded. Preliminary tests showed that the dasher caused

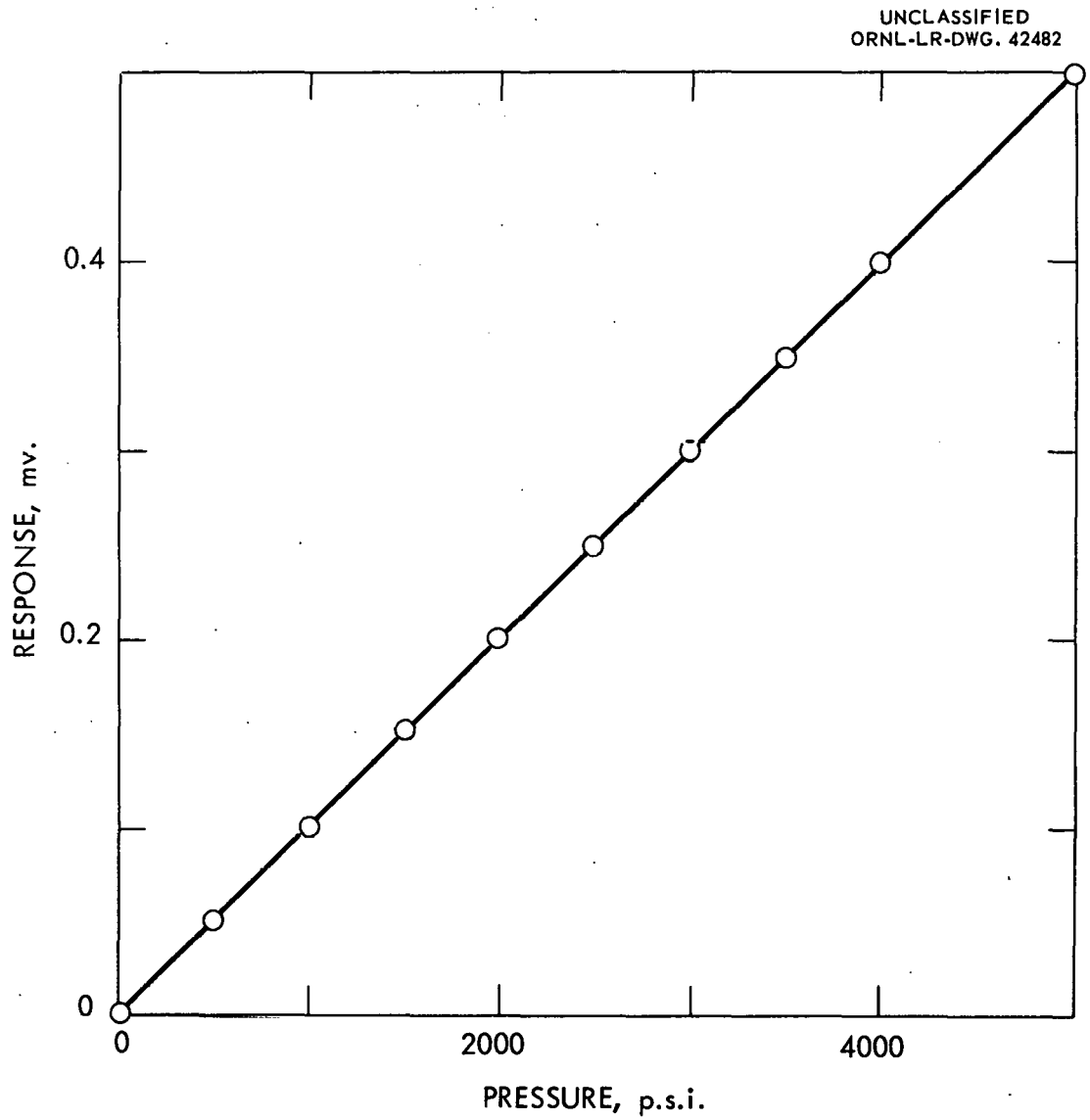

Fig. 12. Response of Baldwin pressure cell.

TABLE IV

PRESSURE CELL CALIBRATION

Dead Weight Load, p.s.i.	Instrument Reading	% Error
500	500	0
1000	1000	0
1250	1250	0
2500	2510	0.4
4500	4525	0.6

a marked acceleration of the reaction rates under measurement. In this technique, coils of wire wrapped around the reaction vessel body were alternately energized, causing a stirrer with a core of soft iron to reciprocate within the vessel, stirring the contents. The acceleration was probably caused by the continual exposure of fresh stainless steel surface as the vessel wall was scraped by the dasher. Efforts to decrease this interference by coating the interior of the autoclave or by changing the material from which the stirrer was fabricated were unsuccessful.

E. Method and Calculations

Since the reaction

$$2\ H_2\ (g) + O_2\ (g) \longrightarrow H_2O\ (l)$$

results in a decrease in the number of moles of gaseous constituents, the course of the reaction was followed readily by measuring the decrease in total pressure, p, of the system as a function of time at a constant temperature. From the initial composition of the gaseous phase and the stoichiometry of the reaction, the partial pressures of hydrogen and oxygen, p_{H_2} and p_{O_2}, at any time, t, can be calculated from the total pressure measurement corrected for the vapor pressure of water, which was assumed to be the saturated steam value. The reaction rate in terms of these experimental values was expected to be of the form

$$-\frac{dp}{dt} = k''w\ p_{H_2}^{a}\ p_{O_2}^{b}$$

where k" is a rate constant, w the weight of catalyst, and a and b are constants. Experimentally, it was found that a = 1 and b = 0, so that the expression became

$$-\frac{dp}{dt} = k''wp_{H_2}$$

By differentiating the expression for the total pressure with respect to time,

$$p = p_{H_2} + p_{O_2} + p_{H_2O}$$

$$\frac{dp}{dt} = \frac{dp_{H_2}}{dt} + \frac{dp_{O_2}}{dt}$$

and substituting the relation

$$\frac{dp_{O_2}}{dt} = \frac{1}{2}\frac{dp_{H_2}}{dt}$$

one can write

$$-\frac{dp_{H_2}}{dt} = k'wp_{H_2}$$

Since the reaction does not take place in the gaseous phase, however, k' calculated from this expression depends on the volume, V, of the gas space.[14] A more correct expression for this type of heterogeneous reaction is

$$-\frac{dn_{H_2}}{dt} = kwp_{H_2}$$

where n_{H_2} is the number of moles of hydrogen. Assuming the ideal gas law, this expression can be rewritten as

$$-\frac{V}{RT}\frac{dp_{H_2}}{dt} = k'wp_{H_2}$$

or

$$-\frac{dp_{H_2}}{dt} = k' \frac{RTw}{V} p_{H_2}$$

Rearranging,

$$-\frac{dp_{H_2}}{p_{H_2}} = k' \frac{RTw}{V} dt$$

Integrating,

$$\log p_{H_2} = \frac{k'RTw}{2.303V} t + C$$

Therefore a plot of log p_{H_2} versus time gives a straight line with a slope of $\frac{k'RTw}{2.303V}$, from which k' can be evaluated. When a stoichiometric gas mixture was used, a plot of log total pressure in excess of steam against time was used since under that restriction the slope is the same. In the closed autoclave system used in this work, the gas phase volume, V, is a function of temperature. Water expands considerably on heating, thus tending to decrease the gas volume. Opposing this is the expansion of the autoclave itself and the increase in the amount of water present as steam. The gas phase volume was calculated from the room temperature volume of the autoclave and the known properties of water[15,16] and type 347 stainless steel.[17] In calculating the gas phase volume, the volume of the pressure capillary (~0.15 ml.), the volume of the water formed during the reaction, and the compressibility of water were neglected, and the catalysts were all assumed to have a constant density of 10 g./ml. Figure 13 is a graph of the free gas volume against temperature. The autoclave volume at room temperature was 13.1 ml., and was determined by

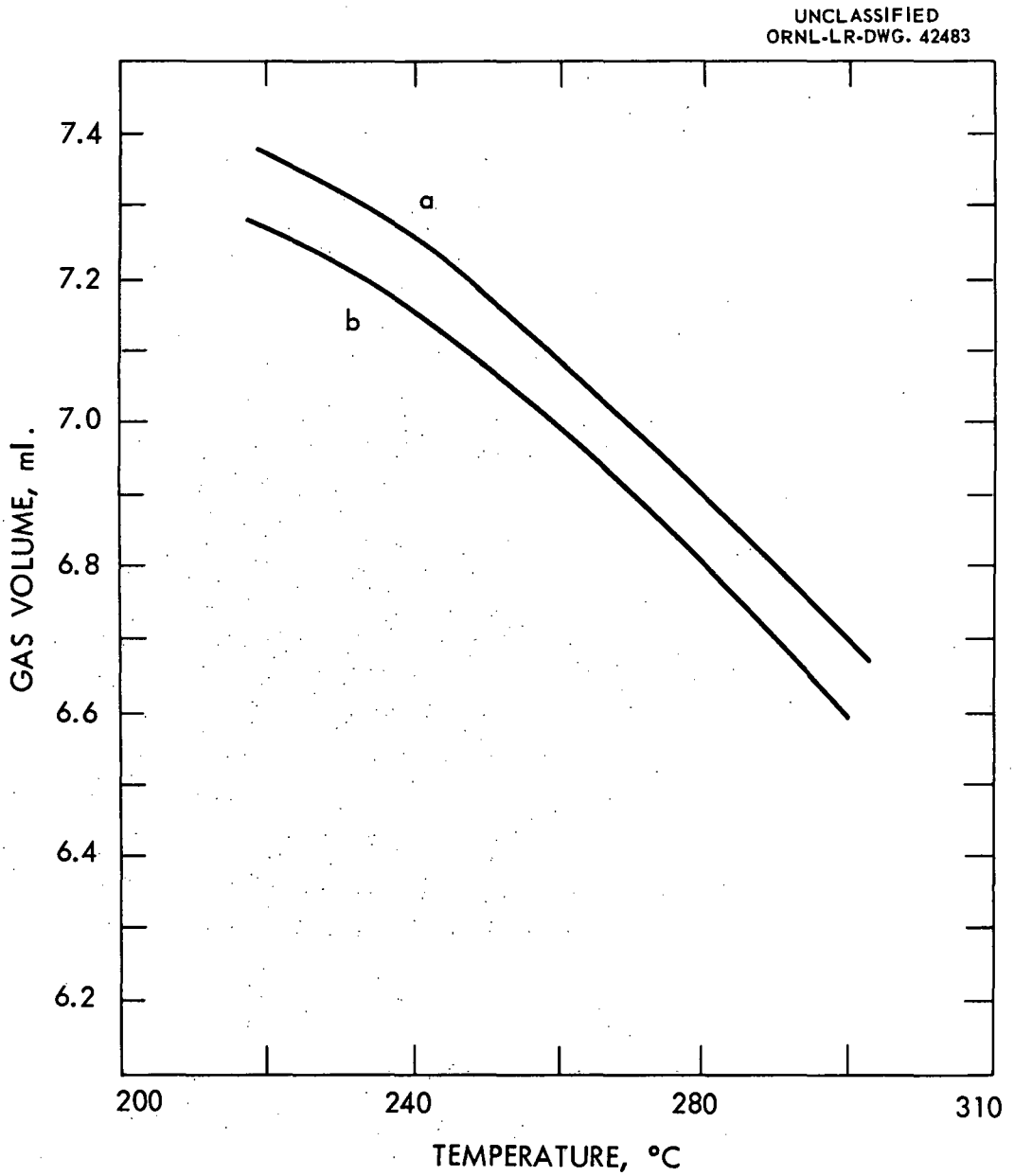

Fig. 13. Gas volume of the reaction vessel as a function of temperature: (a) loaded with 5 ml. of water; (b) loaded with 5 ml. of water and 1 g. of catalyst.

weighing the autoclave empty and filled with water. The measured value agreed with that calculated from the interior dimensions of the closed autoclave.

F. Experimental Procedure

1. Charging

The autoclave was first carefully cleaned and dried. The desired amount of thorium oxide or thorium-uranium oxide mixture was weighed on an analytical balance and carefully transferred to the autoclave, and 5 ml. of distilled water was added by pipette. The autoclave was then closed and the capillary tube connected to the three-way valve at the top of the Baldwin pressure cell. The autoclave was inserted in the heater, the thermocouple connections were made, and a Plexiglas blast shield was placed in front of the apparatus. An oxygen cylinder was connected by means of a 20-mil-I.D. stainless steel capillary tube and high-pressure fitting to the other side of the valve, and, after the entire system had been flushed with oxygen, the desired pressure was obtained by adjusting a high-pressure reducing valve on the gas cylinder. The autoclave valve was then closed, the capillary tube disconnected, a tube from a hydrogen cylinder attached, and, after the lines and valves attached to the gas cylinder had been flushed, the desired hydrogen pressure was obtained similarly.

2. Measuring

The charged autoclave was shaken in the heater at room temperature for an hour or longer to check for leaks and to suspend the solids. If the pressure remained constant, indicating there were no leaks, the heater was turned on and the temperature brought to the desired value. The pressure was then recorded as a function of time at constant temperature until the reaction reached completion or became too slow to measure practically.

CHAPTER III

RESULTS

A. With Water Only

The system was assembled and 5 ml. of water was added to the reaction vessel, which was then closed and heated to various temperatures between 200° and 300°. The vapor pressure of the water was observed and was found in good agreement with handbook values (Table V). This experiment served to verify the system temperature and pressure calibrations as well as to provide the necessary pressure corrections for the kinetic experiments.

The rate of reaction of a stoichiometric mixture of hydrogen and oxygen was then measured in the system loaded with 5 ml. of distilled water to determine a base line for work with slurries. The rates were found to be very slow, in agreement with McDuffie et al.,[5] provided that the reaction vessel was clean and that the stainless steel surfaces were passivated by treatment with nitric acid or oxygenated water at elevated temperatures (see Table VI). Once the steel surfaces were oxidized, cleaning with a cotton swab was effective without damaging the surface covering. Thus, in most cases, the background rate could be ignored, although in some cases the reaction rates over slurries were also very slow and a correction was necessary.

TABLE V

STEAM PRESSURE CALIBRATION

Temperature	Observed Pressure, p.s.i.	Handbook Value, p.s.i.	% Error
218°	312	324	-3.7
230°	392	407	-3.7
252°	590	596	-1.0
278°	900	902	-0.2
288°	1067	1048	+1.8
290°	1090	1079	+1.1
300°	1268	1246	+1.8

TABLE VI

RATE CONSTANTS WITH WATER ONLY

Temperature	k', hr.$^{-1}$	$\bar{k} \times 10^8$ moles H_2/hr.-p.s.i. H_2
256°	0.0023	2.6
266°	0.0016	1.7
284°	0.0022	2.2
287°	0.0010	1.0
290°	0.0020	1.8

Water control tests were run frequently during the experimental work to determine if there were high-temperature leaks or if the autoclave was contaminated.

B. With Thorium Oxide Slurries

1. Dependence on Weight of Thorium Oxide

Seven experiments were run with a stoichiometric mixture of hydrogen and oxygen and 0 to 4 g. of 650° fired thorium oxide slurried in 5 ml. of distilled water to determine the effect on the reaction rate at 290°.

An initial loading of 400 p.s.i. of oxygen and 800 p.s.i. of hydrogen was used in all these experiments, the shaking apparatus was operated at its maximum speed of approximately 320 cycles per minute, and the total pressure was recorded as a function of time.

The log of the total pressure in excess of steam was found to decrease linearly with time, indicating a first-order dependence on total gas pressure (Figure 14). Thus, to determine the effect of the amount of thorium oxide used, first-order reaction rate constants were calculated from the slopes of graphs of the log of pressure in excess of steam against time (see Table VII).

A plot of rate constant against weight of thorium oxide was found to be linear from 0 to 1 g. of thorium oxide in 5 ml. of water but then started curving, indicating that diffusion processes were becoming important (see Figure 15). In all subsequent experiments only 1 g. of

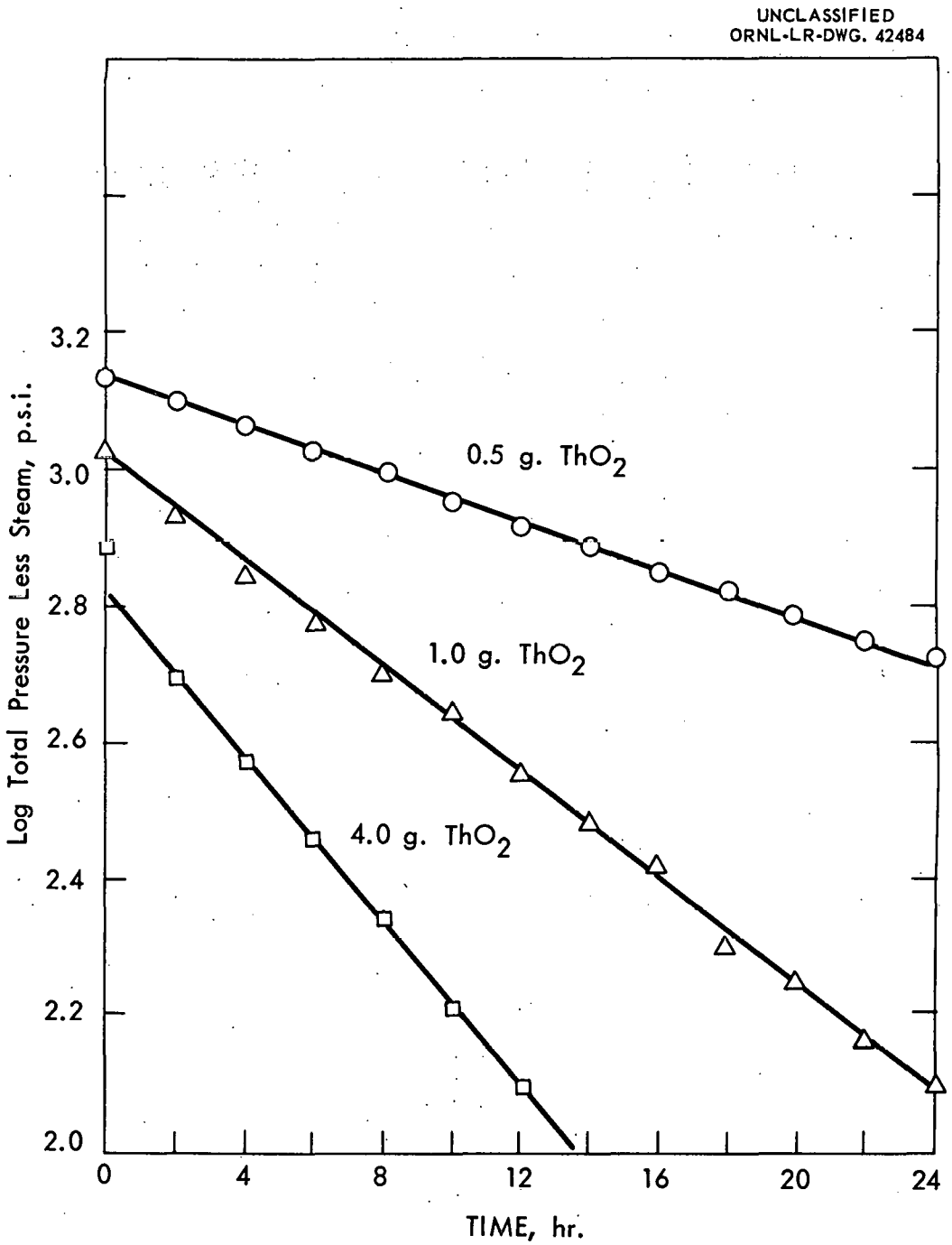

Fig. 14. Typical gas pressure curves showing first-order dependence of the reaction rate at ~ 290°C.

TABLE VII

REACTION RATE CONSTANT FOR VARIOUS WEIGHTS OF THORIUM OXIDE AT 290°C

g. Thorium Oxide/5 ml. Water	k', hr.$^{-1}$	k x 10^8, moles H_2/hr.-p.s.i. H_2
0	0.002	1.8
0.5	0.040	36
1.0	0.076	68
1.5	0.087	78
2.5	0.120	108
4.0	0.138	124

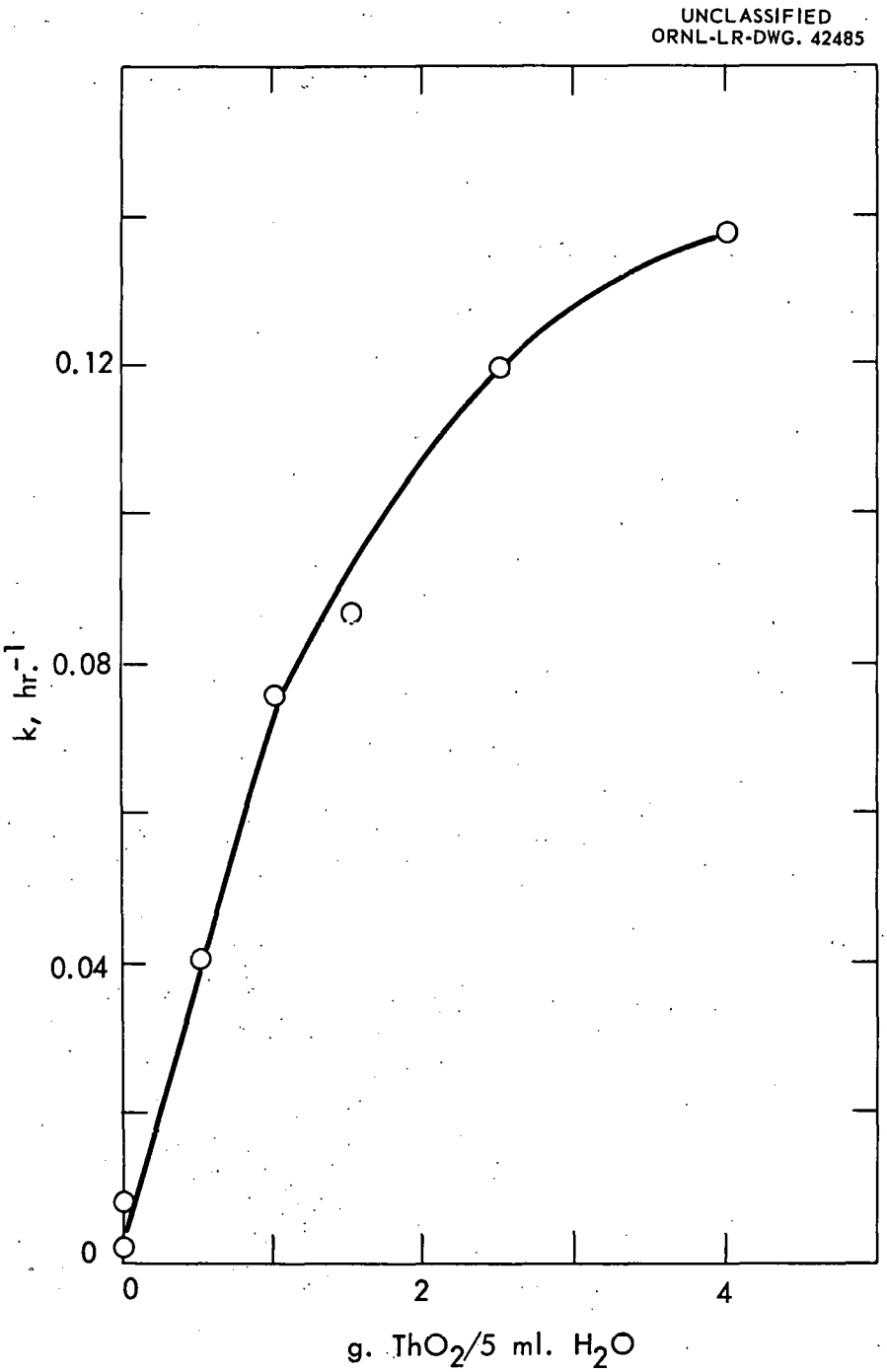

Fig. 15. Observed rate constants for various weights of thorium oxide at 290°.

thorium oxide was used and all tests were run at maximum shaking speed. All rate constants for the remaining work were calculated for 1 g. of solids.

2. Order with Respect to Hydrogen

Four experiments were run with 1.000 g. of 650° calcined thorium oxide in 5.0 ml. of distilled water and a constant initial oxygen pressure of 400 p.s.i. The initial hydrogen pressure was then varied from 350 to 875 p.s.i., and measurements of pressure against time at temperatures near 290° were taken. From these data the partial pressure of hydrogen was calculated as a function of time, assuming that both hydrogen and oxygen behaved ideally and that the only reaction product was water. The half-life for the disappearance of hydrogen was found to be nearly constant regardless of the initial pressure of hydrogen, indicating first-order dependence (Table VIII). First-order rate constants calculated from graphs of the log of hydrogen pressure against time agreed well with those previously calculated from total pressure measurements.

3. Order with Respect to Oxygen

Since the order with respect to total stoichiometric gas pressure in excess of steam is unity, as well as that with respect to hydrogen, the order with respect to oxygen must be zero.

An independent check of this conclusion was made by varying the initial oxygen pressure from 250 to 500 p.s.i. while holding the initial

TABLE VIII

HALF-LIFE OF HYDROGEN AT VARYING INITIAL PRESSURE

Hydrogen Pressure, p.s.i., at t_o	Temperature	$t_{1/2}$ of H_2 hr.
350	290°	11.0
425	288°	11.0
800	291°	10.5
875	291°	10.0

hydrogen pressure constant at 800 p.s.i. A slurry of 1 g. of 650° calcined thorium oxide in 5 ml. of distilled water, and temperatures near 290° were again used. From measurements of total pressure against time, the half-lives for the disappearance of hydrogen and oxygen were calculated (Table IX). Values for hydrogen remained constant and were in agreement with those obtained above, while those for oxygen increased with increasing initial oxygen pressure. A log-log plot of the half-life for the disappearance of oxygen against the partial pressure of oxygen at time zero (taken as the time when constant temperature is attained) gave a straight line with a slope of 1 (Figure 16). Since the slope of such a graph is equal to (1-n), where n is the order of the reaction, the order with respect to oxygen must be zero, as anticipated.

4. Temperature Coefficient

The rate of reaction of hydrogen and oxygen in stoichiometric ratio was measured at various temperatures from 240° to 300° over slurries of 1.000 g. of thorium oxide in 5.0 ml. of distilled water. A rate constant was calculated for each experiment from the slope of a graph of the log of the partial pressure of hydrogen against time. The apparent energy of activation, which in this case includes energies of solution, adsorption, and reaction, was determined from the logarithmic form of the Arrhenius equation,

$$\log k = \log A - \frac{\Delta E_a}{2.303RT}$$

TABLE IX

HALF-LIFE OF OXYGEN AT VARYING INITIAL PRESSURE

Oxygen Pressure, p.s.i., at t_o	Temp.	$t_{1/2}$ of H_2 hr.	$t_{1/2}$ of O_2 hr.
258	288°	11.8	5.7
400	293°	11.2	10.2
440	291°	10.0	10.5
804	288°	10.5	17.5

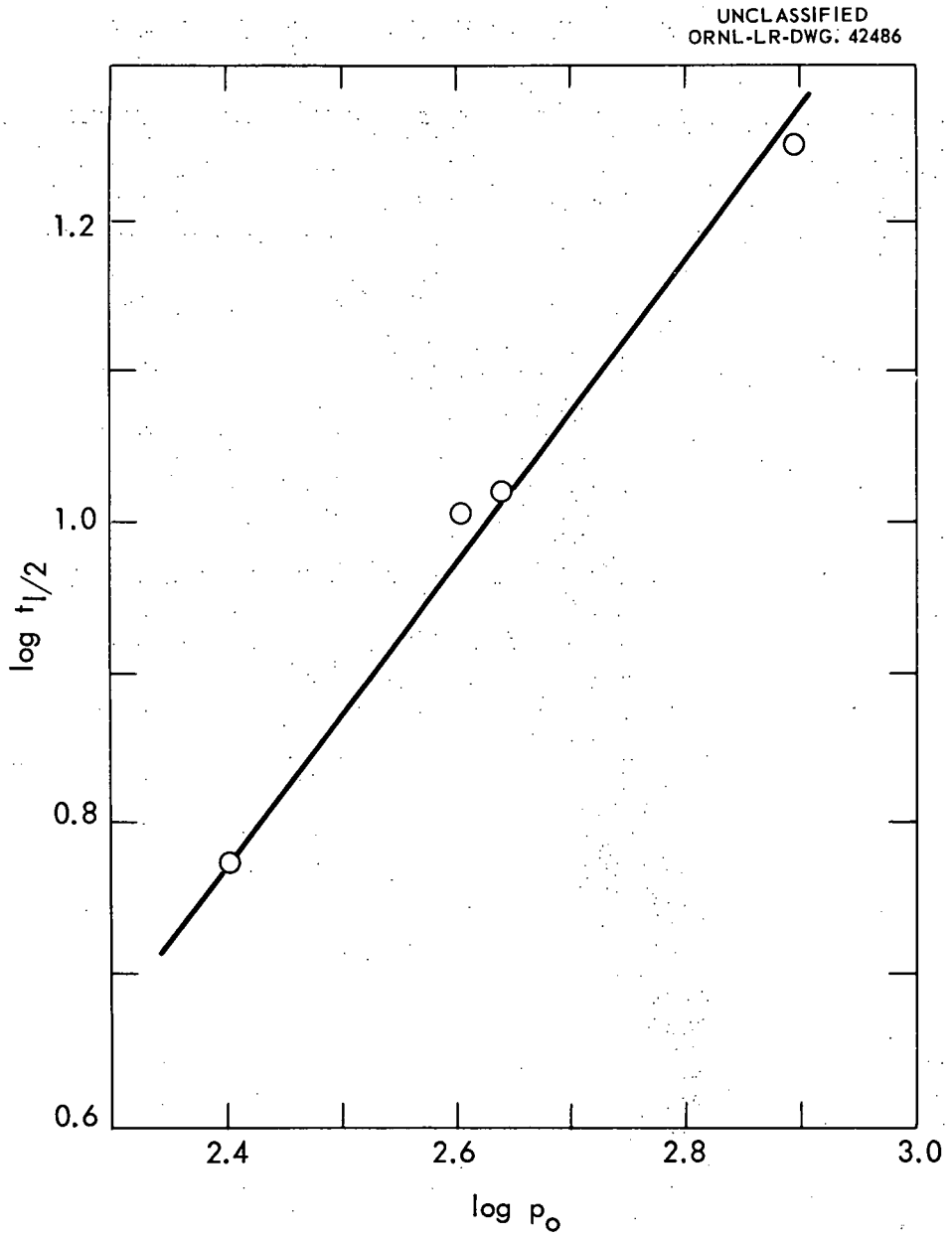

Fig. 16. Log of oxygen half-life as a function of initial partial pressure.

Plots of the log of k against the reciprocal of absolute temperature were made for three series of experiments with thorium oxide calcined at 650°, 800°, and 1000° (Figure 17). Values of ΔE_a were calculated from the slopes of the straight lines obtained. With these values of ΔE_a, the average A factor was calculated for each thorium oxide used. Values for ΔE_a and A are given in Table X.

5. Effect of Specific Surface Area

Calcination of the thorium oxide at temperatures of 650°, 800°, and 1000° gave materials whose specific surface areas were 32.2, 14.3, and 4.8 $m.^2/g.$, respectively. The rate constants mentioned in the paragraph above were recalculated in terms of unit surface area of thorium oxide instead of unit weight and plotted as a function of the reciprocal of absolute temperature (Figure 18). On this basis, the results obtained from the 650° and 1000° material agree very well, indicating linear dependence of rate on surface area. The results from the 800° calcined material, however, do not agree, showing a slightly faster rate per unit surface area.

C. With Thorium Oxide-Uranium Oxide Slurries

1. Dependence on Catalyst Weight

The influence of the weight of the thorium-uranium oxide catalysts on the reaction was not determined. Since the reaction rates observed

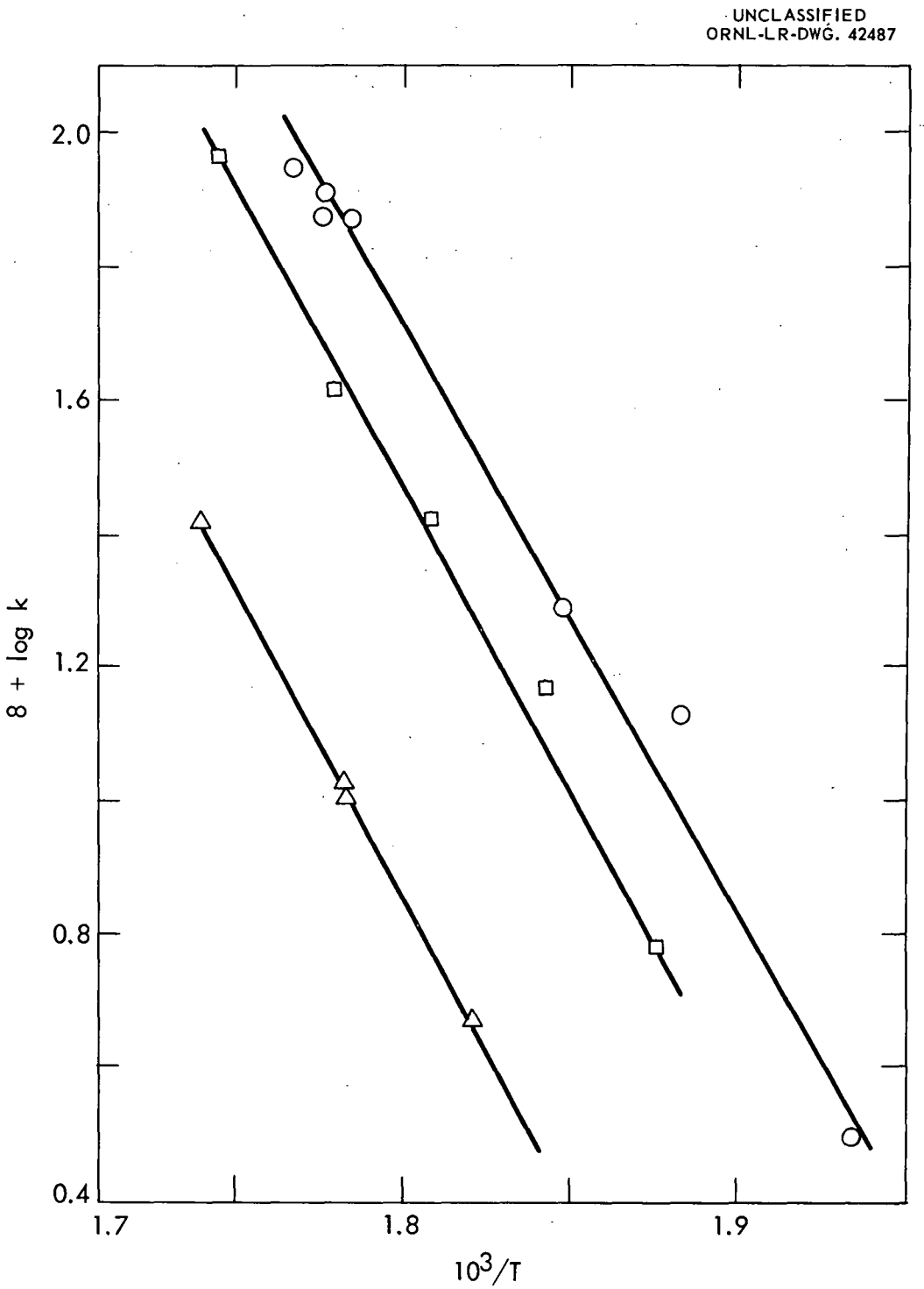

Fig. 17. Arrhenius plots for hydrogen-oxygen reaction catalyzed by thorium oxide calcined at: O, 650°; □ , 800°; Δ, 1000°C; k in moles/p.s.i.-hr.-g.

TABLE X

APPARENT ACTIVATION ENERGIES AND FREQUENCY FACTORS FOR THE REACTION OF HYDROGEN AND OXYGEN CATALYZED BY THORIUM OXIDE SLURRIES

Calcination Temperature	A, moles/p.s.i.-hr.-g.	ΔE_a, kcal./mole
650°	2.7×10^9	40.0
800°	6.8×10^9	41.6
1000°	4.0×10^9	42.6

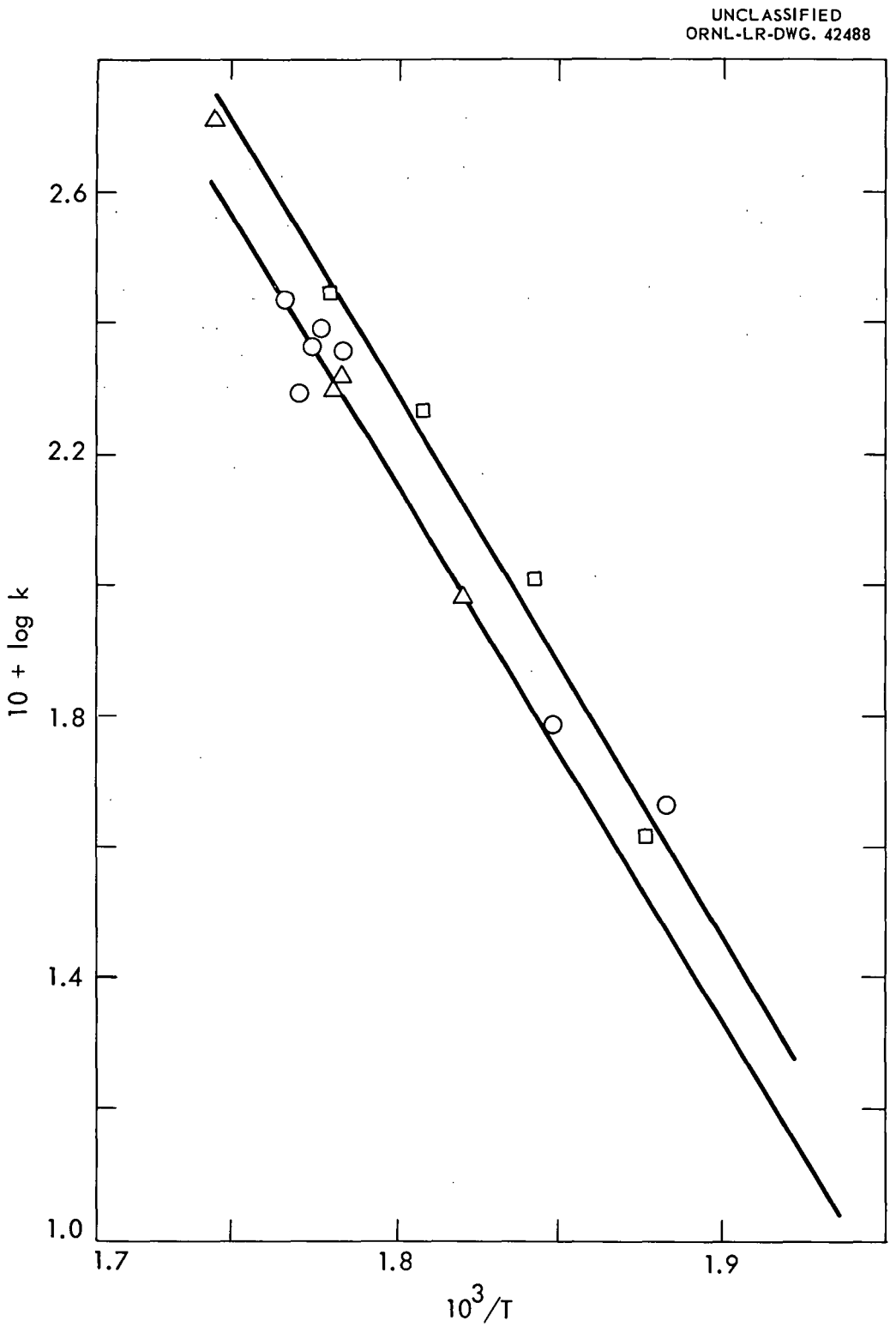

Fig. 18. Arrhenius plots for hydrogen-oxygen reaction catalyzed by thorium oxide calcined at: O, 650°; □ , 800°; Δ, 1000°; k in moles/p.s.i.-hr.-m.^{2}.

were first order with respect to total gas pressure in excess of steam and not much different from those found in the case of pure thorium oxide, a similar dependence on the weight of solids was assumed and all measurements were made with 1 g. of solids in 5 ml. of water with the shaker operating at its maximum speed.

2. Order with Respect to Hydrogen

Three experiments were run near 292° with a slurry of 1 g. of thorium-uranium oxide crystals that had been calcined at 650° suspended in 5 ml. of H_2O. A constant initial oxygen gas pressure of 400 p.s.i. and initial hydrogen pressures of 400, 800, and 1200 p.s.i. were used. From the pressure-time data obtained, the half-life for the disappearance of hydrogen was calculated for each reaction based on the same assumptions as for the thorium oxide catalyzed reaction. The values obtained were essentially constant, indicating first-order dependence on hydrogen pressure. A similar series of experiments with the thorium oxide with adsorbed uranium oxide also gave constant, though somewhat shorter, half-times (see Table XI).

3. Order with Respect to Oxygen

Since the order with respect to both total gas pressure and hydrogen partial pressure was found to be 1, the order with respect to oxygen pressure was taken to be zero. This was verified in the case of pure thorium oxide (see Sect. B-3), and, since the thorium oxide-uranium

TABLE XI

HALF-LIFE FOR HYDROGEN AT VARIOUS INITIAL PARTIAL PRESSURES OVER SLURRIES OF THORIUM OXIDE-URANIUM OXIDE PREPARED BY INDICATED METHOD

Hydrogen Pressure, p.s.i., at t_o	Temperature	$t_{1/2}$ hr.
	A. Coprecipitated Method	
602	292°	13.0
1264	288°	13.2
1660	292°	13.0
	B. Adsorption Method	
667	294°	11.8
1000	294°	11.8
1496	294°	11.7

oxide catalysts acted very similarly, it was not verified again.

4. Temperature Coefficient

The rate of the reaction of hydrogen and oxygen gases in stoichiometric ratio was measured with slurries of 1.000 g. of the thorium oxide-uranium oxide catalysts suspended in 5 ml. of distilled water at temperatures from 248° to 302°. Three series of experiments were made for both catalysts with oxides which were calcined at 650°, 800°, and 1000°. Rate constants were calculated for each experiment from the slope of a plot of the log of the partial pressure of hydrogen against time. An Arrhenius plot was made for each material and values for the apparent activation energies were calculated from the slopes of the lines obtained (see Figures 19 and 20). The results (see Table XII) showed that the activation energies increased with calcination temperature for both materials. Values calculated for the frequency factor also increased with calcination temperature.

5. Effect of Specific Surface Area

The rate constants per gram of catalyst were converted to rate constants per square meter of surface area and replotted (Figures 21 and 22). The effect was to reverse the order of the curves. When plotted as rate constant per gram of catalyst, they decreased as the calcination temperature of the catalyst was increased with one exception, but when calculated on the basis of unit surface area they increased.

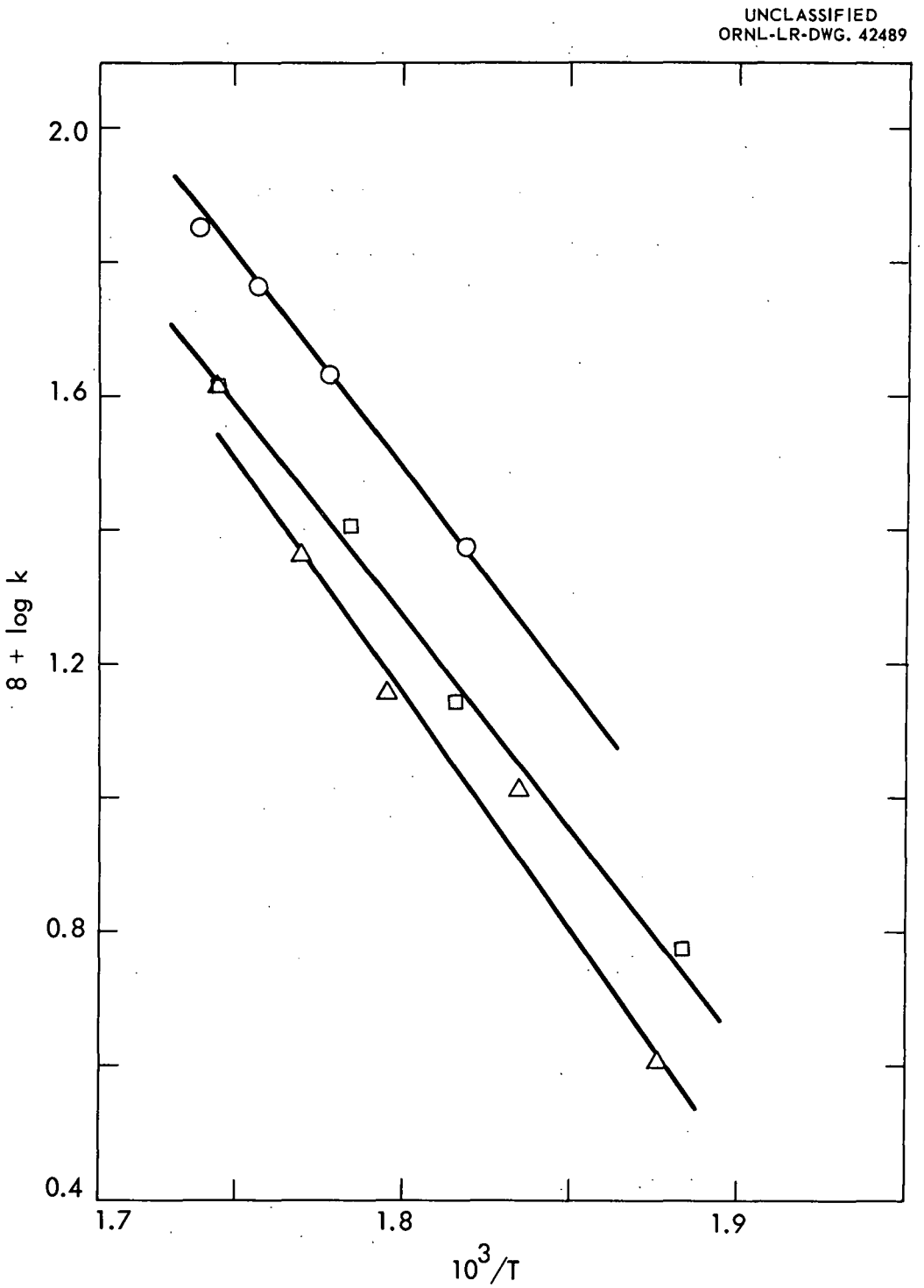

Fig. 19. Arrhenius plot for hydrogen-oxygen reaction catalyzed by thorium-uranium oxide mixed crystals, calcined at: O, 650°; □ , 800°; Δ, 1000°; k in moles/p.s.i.-hr.-g.

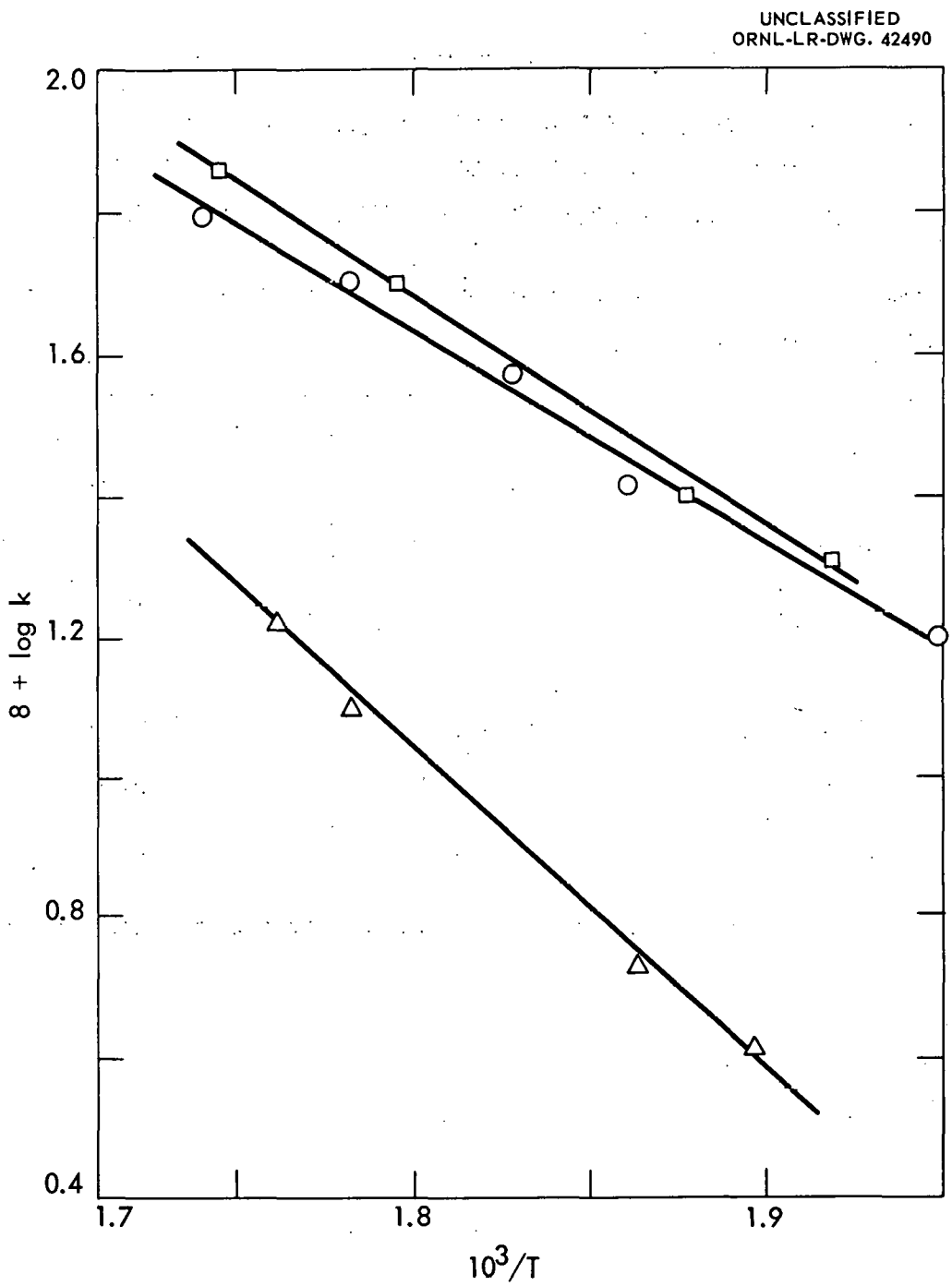

Fig. 20. Arrhenius plot for hydrogen-oxygen reaction catalyzed by thorium oxide with adsorbed uranium oxide calcined at: O, 650°; □, 800°; Δ, 1000°; k in moles/p.s.i.-hr.-g.

TABLE XII

APPARENT ACTIVATION ENERGIES AND FREQUENCY FACTORS FOR THE REACTION OF HYDROGEN AND OXYGEN CATALYZED BY SLURRIES OF THORIUM-URANIUM OXIDE PREPARED BY INDICATED METHOD

Calcination Temperature of Catalyst	A, moles/p.s.i.-hr.-g.	ΔE_a, kcal./mole
	A. Coprecipitation Method	
650°	9.9×10^4	29.3
800°	5.1×10^5	31.6
1000°	6.1×10^5	32.0
	B. Adsorption Method	
650°	0.11	13.7
800°	0.28	14.6
1000°	17.0	20.8

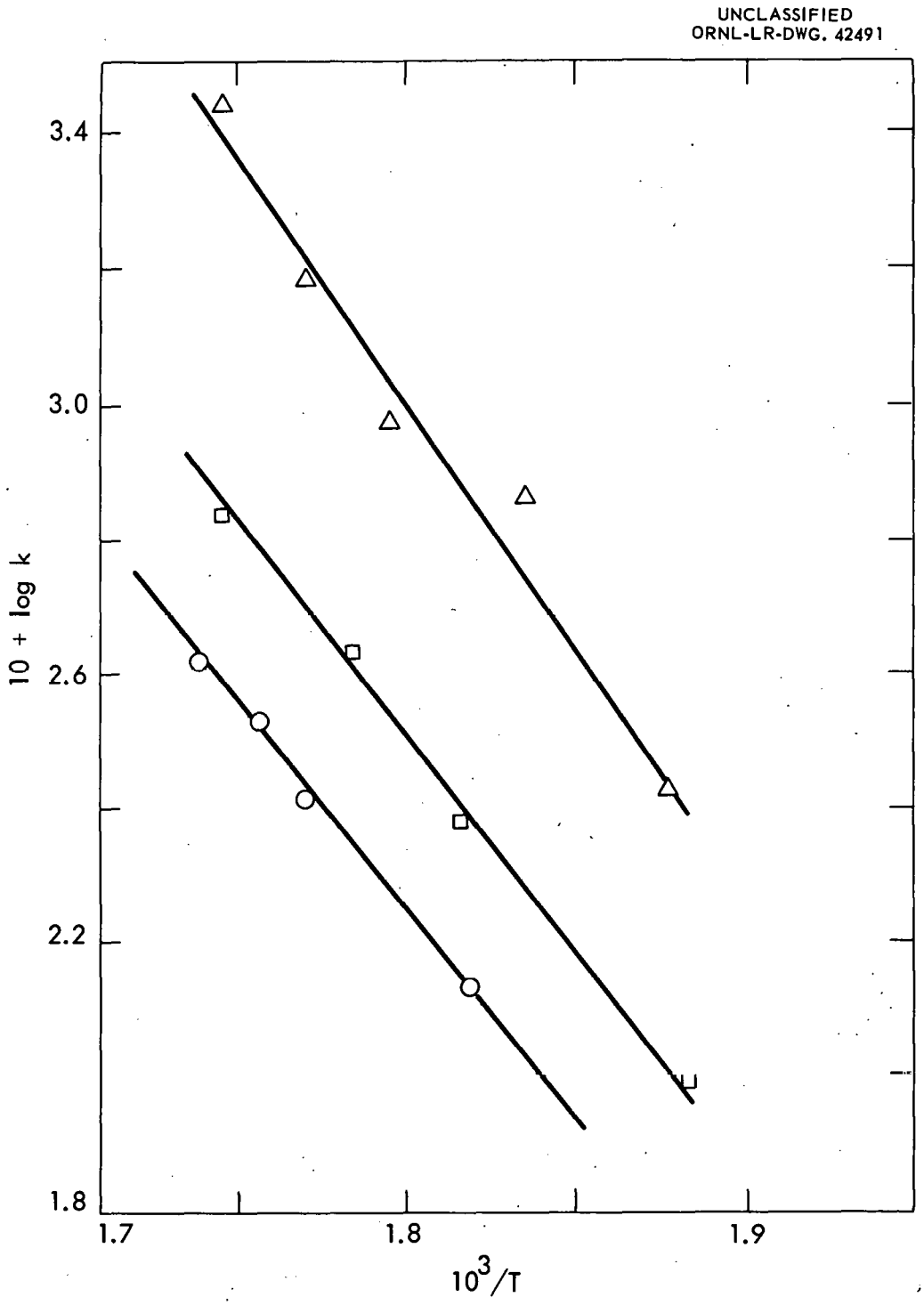

Fig. 21. Arrhenius plots for the hydrogen–oxygen reaction catalyzed by thorium–uranium oxide mixed crystals calcined at: O, 650°; □ , 800°; Δ, 1000°; k in moles/hr. - p.s.i. - m^2.

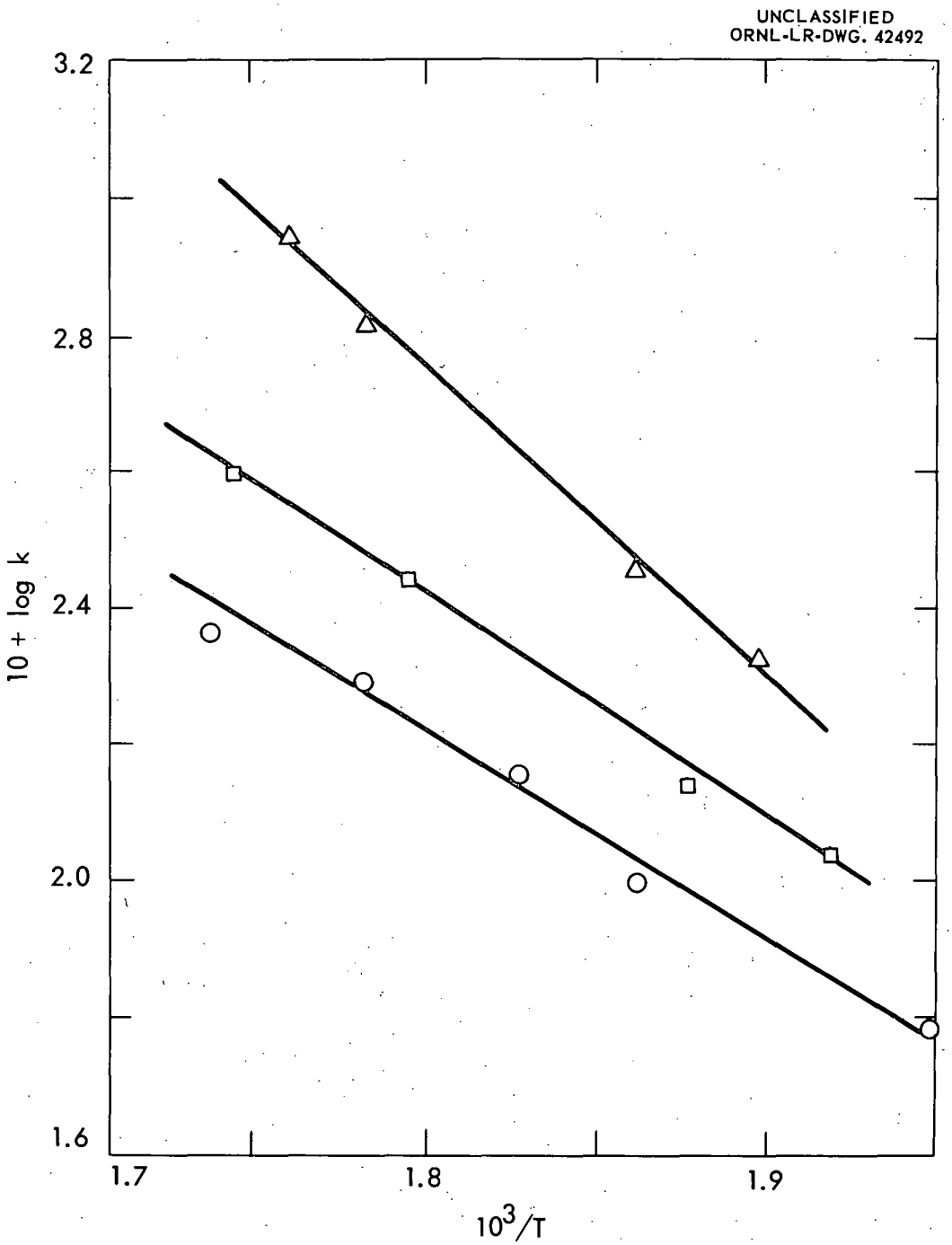

Fig. 22. Arrhenius plots for the hydrogen-oxygen reaction catalyzed by thorium oxide with adsorbed uranium oxide calcined at: O, 650°; □, 800° Δ, 1000°; k in moles/p.s.i.-hr.-m.^{2}.

D. With Uranium Oxide Slurries

Experiments were made with slurries containing only uranium trioxide to compare with the thorium oxide-uranium oxide combinations. A direct comparison is not possible since uranium trioxide by itself is not stable at the temperatures at which the combined catalysts were calcined.[18] Unlike thorium oxide, uranium trioxide shows several crystalline modifications and has a comparatively low surface area. In fact, the measured surface areas of 0.4 $m.^2/g.$ agree well with the geometric surface area calculated from typical crystal dimensions of either the rod or plate forms.[19] The picture was further complicated by the fact that under the conditions of the kinetic experiments the uranium was partially reduced, as evidenced by a color change from yellow to olive. The reduction altered the rate at which hydrogen and oxygen recombined, and the rate was faster at the beginning of an experiment than at the end (Figure 23), the difference being greater the higher the temperature, and disappearing at 260°.

In these experiments some color was noted in the supernatant of the slurry, indicating the presence of a soluble impurity. Upon investigation, a nitrate content of 0.4 per cent was found. To see if the nitrate was having an effect on the reaction rate of the hydrogen and oxygen, 10 g. of the material was washed repeatedly with boiling water until no color appeared in the wash. The nitrate content was decreased by a factor of 10, but the catalytic activity was not affected. One test

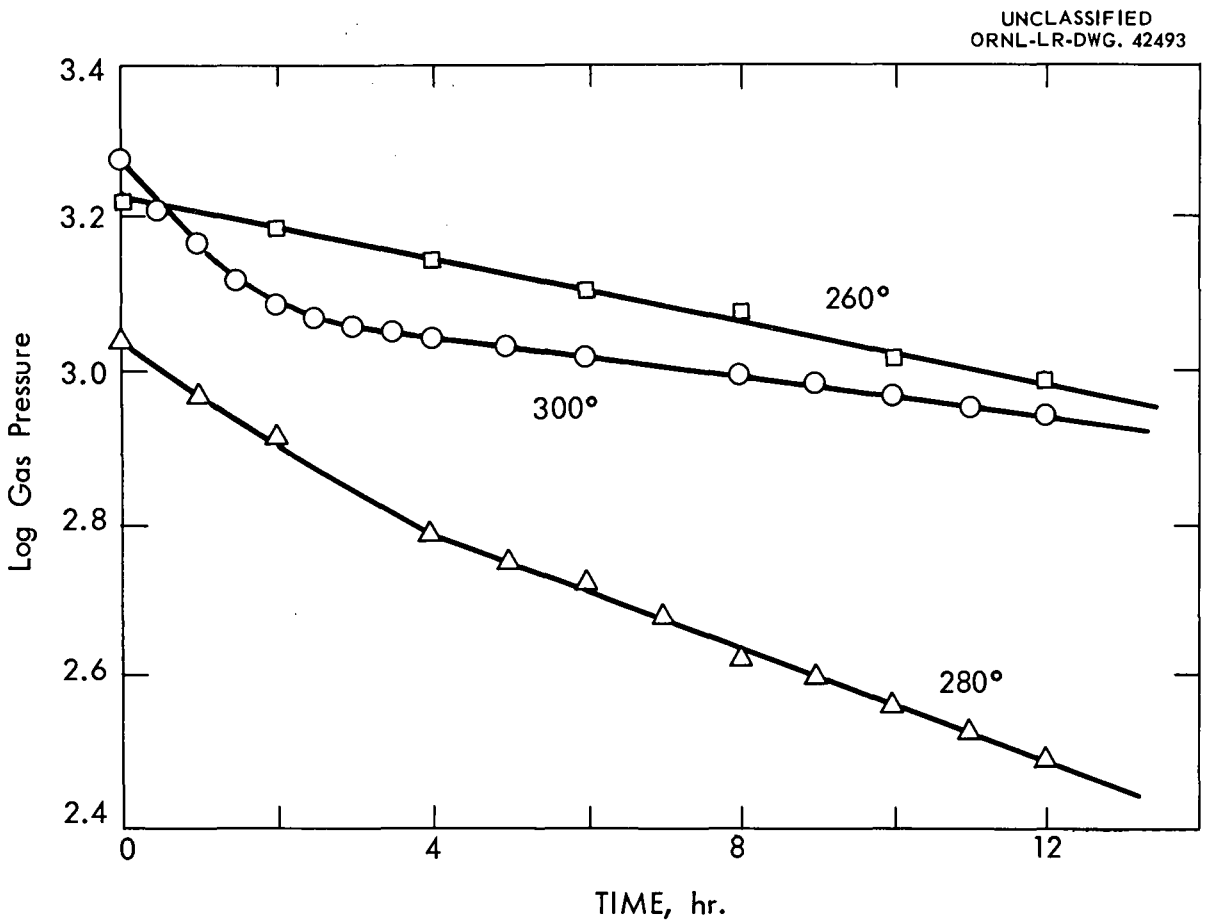

Fig. 23. Log of pressure as a function of time for hydrogen-oxygen reaction over uranium oxide slurries.

was made with a different source of oxide containing less than 10 p.p.m. of nitrate, and again the catalytic activity was not affected although the catalyst surface was reduced more rapidly as evidenced by the change from a fast to a slow rate. Reduction of the weight of catalyst used also resulted in a shortening of the fast reaction period, indicating that the catalyst was being changed during the early portion of the reaction. To verify this a series of experiments was made with a slurry of 1.000 g. of uranium trioxide in 5 ml. of water. The slurry was first used to catalyze the hydrogen-oxygen reaction at 276°C. The reaction was initially fast and after a few hours slowed down as expected. The autoclave was cooled, vented, recharged with a stoichiometric mixture of hydrogen and oxygen, and again heated to 276°C. This time no fast rate was observed initially. In a third test with the same slurry at a temperature of 254° the rate was extremely slow. From the above tests it was concluded that the fast initial reaction occurs on the uranium trioxide surface which is being simultaneously reduced at a rate dependent on the temperature. At 260° the rate of reduction is so slow that it does not interfere with the kinetic measurements, but as the temperature is increased it interferes, causing a decrease in rate. The rate of the hydrogen-oxygen reaction is slower on the reduced surface, although the temperature coefficient of the reaction stays about the same. The initial rates are plotted in Figure 24 according to the Arrhenius relation. The rates of reaction catalyzed by the reduced species from

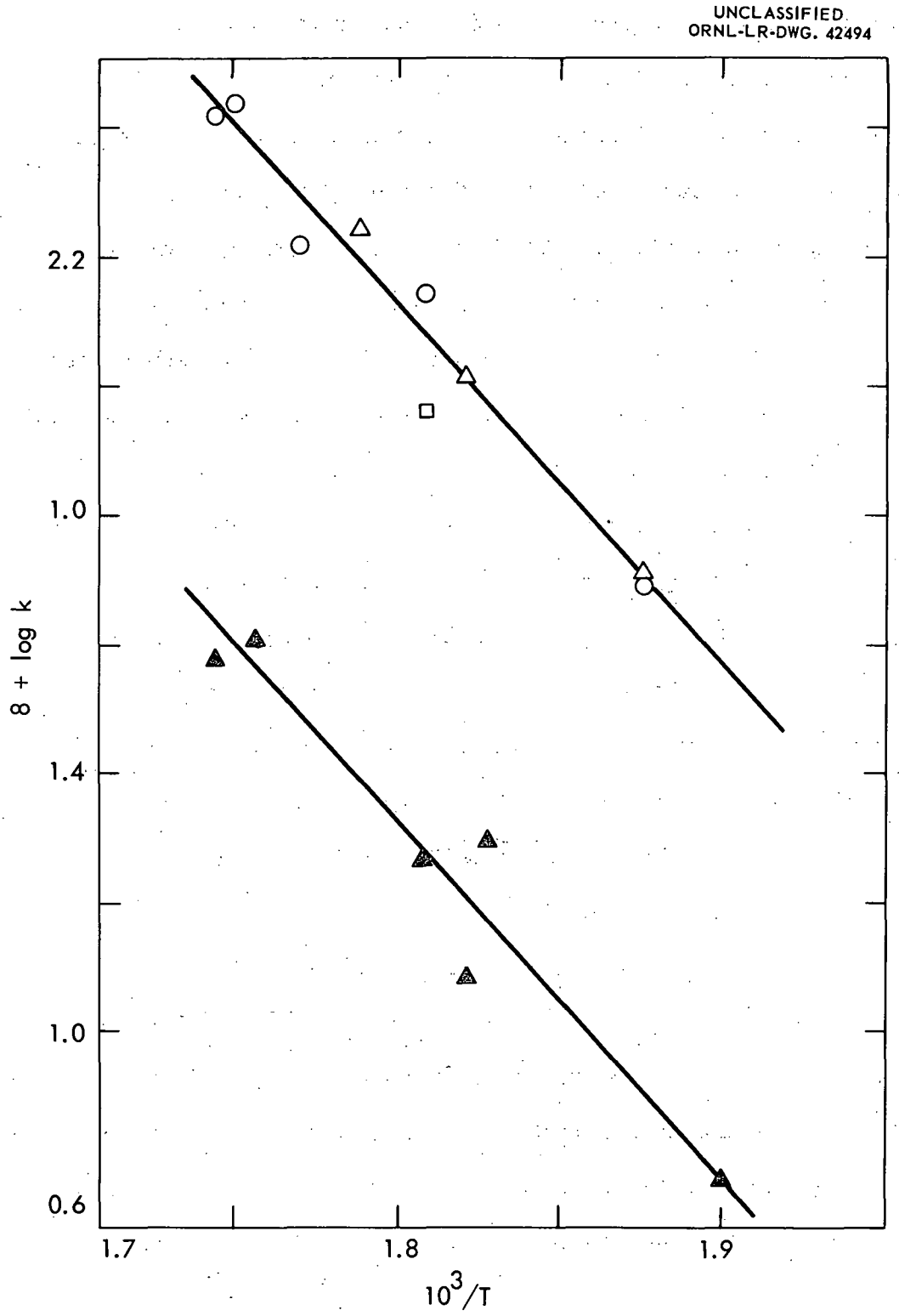

Fig. 24. Arrhenius plots for hydrogen-oxygen reaction catalyzed by uranium oxide slurries. Initial rate with material containing: ○, 0.4%; △, .04%; □, < 10 p.p.m. nitrate, ▲, rate after surface reduction.

the last series of experiments are also plotted. The activation energy for both cases is about 26 kcal./mole, with frequency factors of 2.24×10^4 and 2.51×10^3 moles/p.s.i. H_2-hr.-g., respectively. Previous work on uranium trioxide slurries has been reported[20] as showing first-order dependence on total pressure with an activation energy of 18-19 kcal./mole. The apparatus used incorporated an electromagnetically driven stirrer similar to that rejected in this work because of its effect on the reaction rate. Insufficient data were reported to make a comparison of rate constants.

CHAPTER IV

DISCUSSION OF RESULTS

The results of the measurements of the rate of the hydrogen-oxygen reaction catalyzed by aqueous slurries of thorium oxide, thorium-uranium oxide mixed crystals, and thorium oxide with uranium adsorbed on its surface show that per unit of surface area the mixed crystals calcined at 800° and 1000° are approximately two and six times as effective as thorium oxide by itself. When calcined at 650° the rates are comparable. The thorium oxide with adsorbed uranium oxide calcined at 650° and 800° is more effective than thorium oxide alone at temperatures below 290° where the Arrhenius lines cross because of the difference in temperature dependence. With material calcined at 1000° the crossover temperature obtained by extrapolation is of the order of 370°. With both the uranium-bearing materials, increasing the calcination temperature of the catalyst increased its effectiveness. For thorium oxide itself the effect, if any, was very small.

All the reactions were observed to be independent of the oxygen pressure and dependent on the first power of the hydrogen pressure in the temperature and pressure range covered. This indicates a mechanism in which the active surface is always saturated with oxygen and the rate is controlled by the rate at which hydrogen atoms approach the surface. In such a situation it may be postulated either that the reaction occurs

on the surface between adsorbed oxygen and adsorbed hydrogen where the hydrogen coverage is sparse compared to the oxygen (Langmuir-Hinshelwood mechanism) or that reaction occurs directly between adsorbed oxygen and molecular hydrogen in solution (Rideal mechanism).[21]

In the first case it may be assumed that the Langmuir isotherm applies since the solubility of the gases in water is small and hence approximates gaseous behavior. Then the rate expression is given by the relation

$$-\frac{dn}{dt} = kS\sigma_{H_2}\sigma_{O_2}$$

where k is the rate constant, S is the surface of the catalyst available for gas adsorption, and σ_{H_2} and σ_{O_2} are the fractions of the available surface covered by hydrogen and oxygen, respectively. It is assumed that the amount of water adsorbed stays constant and does not affect the kinetics other than by decreasing available surface. In the absence of water the reaction proceeds explosively at ~250°C. If it is further assumed that the surface is always saturated with respect to oxygen, σ_{O_2} becomes constant, and

$$-\frac{dn}{dt} = k'\sigma_{H_2}$$

The fraction of surface covered by hydrogen according to the Langmuir isotherm is given by

$$\sigma_{H_2} = \frac{Kp_{H_2}}{1 + Kp_{H_2}}$$

where K is the equilibrium constant for hydrogen adsorption. Using solution concentration instead of partial pressure and assuming that K is small compared to unity,

$$\sigma_{H_2} = KC_{H_2}$$

Further, if Henry's Law applies,

$$C_{H_2} = ap_{H_2}$$

where a is a constant, and hence

$$-\frac{dn}{dt} = k'\sigma_{H_2} = aKp_{H_2} = k''p_{H_2}$$

which gives the experimentally observed first-order dependence on hydrogen alone. The assumptions of small K and the application of Henry's law seem reasonable in view of the negligible adsorption of gaseous hydrogen on urania surfaces at temperatures below 400°[22] and the applicability of Henry's law found for both hydrogen and oxygen in water to pressures of 500 p.s.i. and temperatures to 315°.[23]

If the rate is controlled by the arrival of dissolved hydrogen molecules at the solid with its adsorbed layer of oxygen, the assumption of Henry's law for hydrogen also leads directly to first-order dependence on hydrogen pressure. Whether the hydrogen reacts as a molecular species in solution or as an adsorbed species cannot be determined from the data and is of little practical consequence.

A more interesting result is the correlation of the frequency factors and apparent activation energies of the various catalysts. It

has been observed in many cases of heterogeneous catalysis involving series of similar catalysts that a change in activation energy is frequently accompanied by a change in frequency factor such that the rates tend to remain constant.[24] This effect is known as the compensation effect and applies to the catalysts investigated here. Empirically, it is found that the relation

$$\log A = \frac{\Delta E_a}{a} + c$$

usually exists, where a and c are constants. Figure 25 is a graph of log A against ΔE_a for all the catalysts tested. It is seen that the relation holds rather well, regardless of composition or calcination temperature, for all the catalysts except the uranium oxide by itself, which, as previously pointed out, is not comparable to the other materials.

This effect may be explained by considering the reaction as taking place on different active sites, in this case perhaps thorium atoms and uranium atoms. The thorium atom sites are characterized by a high activation energy, ΔE_1, and the uranium sites by a lower activation energy, ΔE_2. The overall rate constant is then given by

$$k = A_1 e^{-\Delta E_1/RT} + A_2 e^{-\Delta E_2/RT}$$

If the two terms on the right hand side are assumed to be of the same order of magnitude and ΔE_1 is much larger than ΔE_2, it is apparent that A_1 must be much larger than A_2. While an Arrhenius plot for such

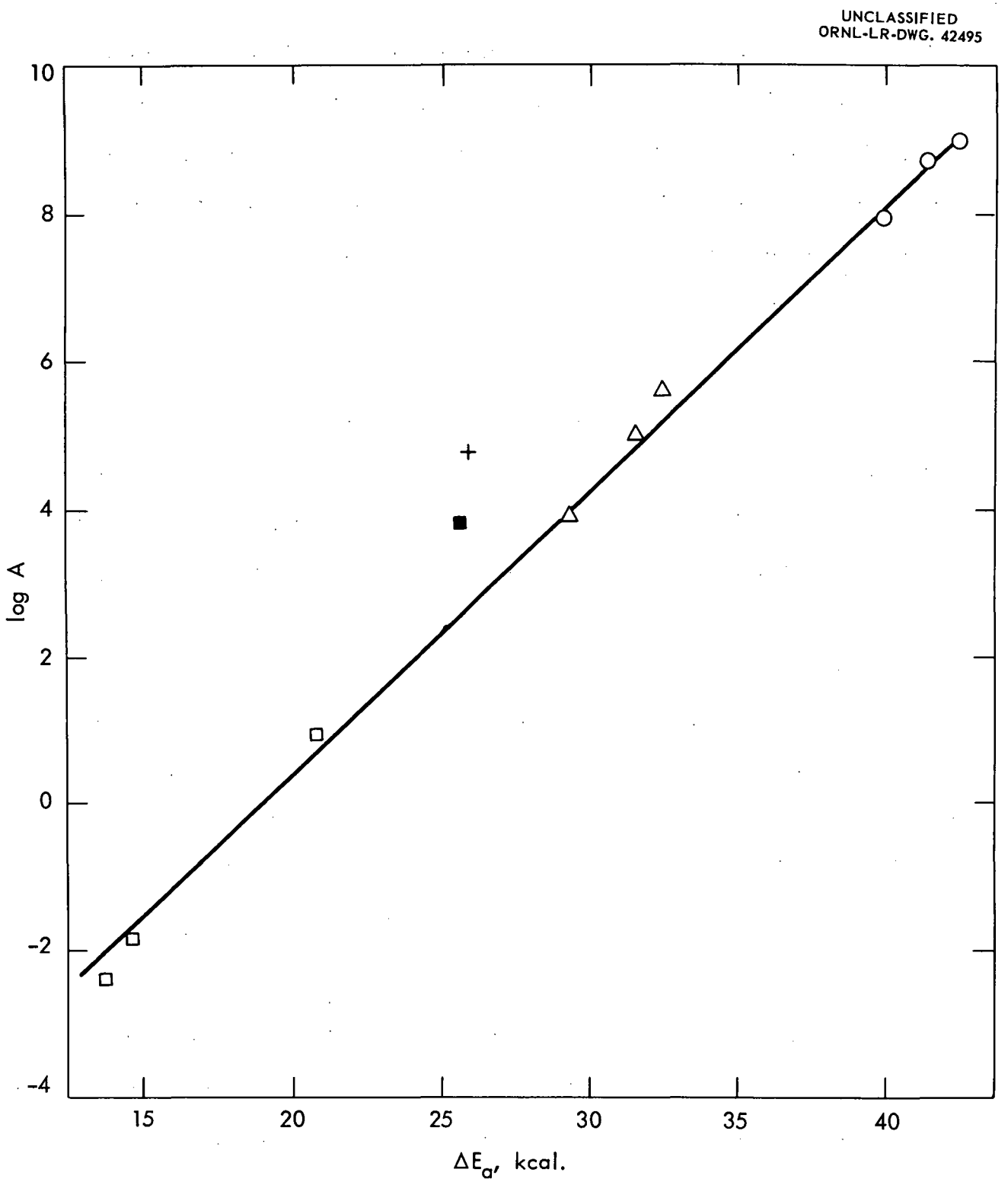

Fig. 25. Compensation effect for reaction of H_2 with O_2 over thorium oxide, O; thorium-uranium oxide mixed crystals, Δ; thorium oxide with adsorbed uranium oxide, □ ; uranium trioxide, initial, +; final, ■ .

an expression is not a straight line, it may appear to be over a limited temperature range such as was used in this work. The constants ΔE_1 and A_1 can be assumed to be of the order of 42 kcal. and 10^9, respectively, as obtained for the thorium oxide alone, the small differences being ascribed to impurities and experimental error. If very pure materials were used, the small compensation effect with calcination temperature changes might well disappear.[24] The constants A_2 and ΔE_2 cannot be evaluated without knowing considerably more about the nature of the catalyst surfaces, such as the number of sites of the second kind, their relation to the uranium oxidation state, and the effect of calcining on their distribution. The relative adsorption of water on the different sites could also be involved. Qualitatively, however, Figure 25 can be explained on the basis of the number of uranium sites to be expected on the surface. When prepared by coprecipitation, the uranium is probably more uniformly distributed throughout the particle, whereas when the uranium trioxide is incorporated onto the catalyst by adsorption it is principally on the surface. Therefore, for roughly equal amounts of uranium added, more sites of the second kind should appear on the adsorbed material, as is observed. Calcination of this material at 1000° results in diffusion of the uranium into the particle, reducing the concentration of these sites as indicated by the increase of A and ΔE_a. By this criterion, in the case of the material prepared by coprecipitation, there also seems to be some tendency for the thorium to preferentially occupy

surface sites. Investigation of the surface by infrared techniques[25] could perhaps lead to quantitative interpretation of these results.

CHAPTER V

SUMMARY

Aqueous slurries of thorium oxide and thorium oxide containing uranium were investigated for their catalytic activity for the reaction of hydrogen and oxygen to form water. Pure thorium oxide, thorium-uranium oxide mixed crystals prepared by calcining coprecipitated oxalates, and thorium oxide with uranium oxide sorbed on the surface were used after calcining at 650°, 800°, and 1000°. The reaction rates were found to be first order with respect to hydrogen pressure and zero order with respect to oxygen pressure in all cases at temperatures from 230 to 300° and total gas pressures from 100 to 2000 p.s.i. For the pure thorium oxide an average activation energy of 41 kcal./mole and an average frequency factor of 4.6×10^8 moles/p.s.i. H_2-hr.-g. of ThO_2 were found which did not change much with calcination treatment. Addition of uranium lowered both ΔE_a and A, the maximum effect giving a ΔE_a of ~14 kcal. with an A of $\sim 10^{-2}$. In spite of this large variation, actual rates for all catalysts were within one order of magnitude when compared on a unit surface area basis. The 1000° calcined thorium-uranium oxide mixed crystals were the most active between 260° and 300°. At lower temperatures the 1000° fired thorium oxide with adsorbed uranium was slightly superior. The data were explained on the basis of a mechanism involving a saturated layer of adsorbed oxygen with hydrogen as slightly

adsorbed or in solution. A compensation effect was noted and explained on the basis of a two-site process, one site being related to the uranium concentration on the catalyst surface and the other characteristic of pure thorium oxide. A few tests on uranium trioxide slurries gave initial fast rates followed by slow ones, the change being accompanied by reduction of the surface under the experimental conditions. The apparent activation energy for both surface conditions was 26 kcal./mole based on first order rate constants with frequency factors of 2.2×10^4 and 2.5×10^3 moles/p.s.i. H_2-hr.-g. for the initial and final rates, respectively.

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